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VOL. 46 NO. 434 FEBRUARY 1960

THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 2 December 1959, the Chair being taken by C. S. Newey, a member of Council.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman introduced the authors and Dr J. Marechal then presented the following paper in summary.

SOME ASPECTS OF UREA DEWAXING OF MIDDLE AND HEAVY DISTILLATES *

By J. MARECHAL † and P. de RADZITZKY †

SUMMARY

After a short review of the literature on the principles of urea adduction, this paper discusses laboratory investigations on the use of urea as a dewaxing agent for middle and heavy distillates. Using a Middle East wax distillate the operating conditions were studied. The results demonstrate the superiority of the urea process over conventional solvent treatment for lowering the pour point of light lubricating oils.

Preparation of solvent neutral lubricating oils by a combination of operations involving urea dewaxing is also discussed. The feedstock, after phenol refining, is submitted to two treatments: (*a*) a conventional solvent dewaxing followed by urea dewaxing; (*b*) a simple urea dewaxing followed by addition of a pour point depressant. It is shown that solvent neutral lubricating oils can be obtained by simple urea dewaxing, with or without addition of depressant, provided that the desired pour points are not too low.

When the urea dewaxing of petroleum fractions is carried out with deficient urea, ‡ a selectivity in the removal of *n*-paraffins, on the basis of their size, is achieved. This selectivity, as observed by the congealing point of *n*-paraffin extracts with deficient urea, is confirmed by a gas chromatographic study. The principle of selectivity is applied to lowering the pour point of a gas oil. It suggests that in order to obtain a given pour point it is more favourable to dewax a whole fraction with a small amount of urea than to dewax thoroughly part of a fraction and mix the latter with the untreated portion. This viewpoint has been confirmed in studying the lowering of the pour point of a gas oil.

INTRODUCTION

UNTIL now the most widely used separation technique in petroleum processing has been distillation, which permits fractionation of molecules according to their size. The ever growing demand for still better defined products requires the use of complementary means of separation. Liquid : liquid extraction and to a lesser extent selective adsorption are very useful for the segregations based on the class of the molecules. A more recent separation technique, extractive crystallization, offers the possibility of separating molecules according to their shape and to some extent to their size. Among these, urea adduction,[1-3] is used in refining operations for the extraction of molecules having a straight-chain configuration. Other extractive crystallization techniques, such as the formation of inclusion compounds and clathration, which make possible the separation of isomers, are the subject of laboratory studies.[4] The separation of molecules on the basis of their shape can also be achieved by selective adsorption with molecular sieves.[5] This technique is useful mainly for extracting the relatively short normal paraffins present in low boiling petroleum fractions, whereas urea adduction is more suitable for larger molecules.

Urea adduction, discovered twenty years ago by Bengen [1] was studied first at the Badische Anilin und Soda–Fabrik.[6, 7] The disclosure after the war of Bengen's important discovery aroused much interest, investigations were undertaken in many laboratories throughout the world,[2, 3] and several urea dewaxing units have gone into commercial operation during the last few years.[3] The principle of urea adduction is simple. When urea crystals are brought into contact with a mixture of hydrocarbons containing straight-chain components, these are selectively absorbed by formation of a stable crystalline complex separable by filtration. X-ray studies [2] indicate that the crystal structure of urea changes from a tetragonal to a hexagonal system during the complex formation process. The urea molecules wrap around the straight-chain molecules in a hexagonal spiral; the spirals form channels having a diameter of approximately 5 Å, large enough to accommodate straight-chain molecules but not branched chain or cyclic molecules.

The quantity of urea required for the formation of an

* MS received 11 September 1959.

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‡ Throughout this paper the phrase "deficient urea" is used to express amounts of urea less than the optimum quantity.

adduct with a straight-chain hydrocarbon is given by the equation:

$$m = 0{\cdot}65\ n + 1{\cdot}5$$

where m and n represent respectively the mol ratio of urea to hydrocarbon and the number of carbon atoms in the hydrocarbon. This corresponds to 3·5 g of urea/g of hydrocarbon. The presence of an activator is necessary for the formation of the complex to proceed at a suitable rate. Methanol, methylethylketone, acetone, and some other organic solvents are well known as activators. Several factors involved in conventional crystallization are known to influence the formation of adducts: such are seeding, crystal growth inhibitors, crystal dimensions, rates of diffusion, etc. A recent study [8] of adduct formation between solid urea and normal octane vapour shows the influence of these factors and gives a better understanding of the mechanism of adduct formation. The rate of formation of adducts between urea and linear hydrocarbons is of the order of one hour to reach completion.[9] It is worth mentioning that the use of a colloid mill for stirring permits the reduction of the contact time to a fraction of a second, yet with appreciable yields.[10, 11]

The adduction between urea and a straight-chain hydrocarbon is accompanied by an important heat evolution proportional to the length of the chain. The heat of formation is approximately 1·6 kg calorie per carbon atom [9] (the carbon atoms of each extremity of the chain are not taken into account). The magnitude of the heat evolved during adduction is roughly twice as high as the heat of fusion and 30 per cent greater than the heat of vaporization per carbon atom of a hydrocarbon, but is lower than the heat of adsorption per carbon atom of a hydrocarbon on a solid surface. The energy liberated on adduct formation is due mostly to the shortening of the hydrogen bonds during the process of transformation of urea from the tetragonal to the hexagonal configuration.

The decomposition of the adducts can be represented by the following equation [12, 13]:

$$\text{adduct} \overset{K}{\rightleftharpoons} n\text{-paraffin} + m\ \text{urea}$$

where m, the mol ratio of urea to hydrocarbon, is related to the number of carbon atoms n by the relation $m = 0{\cdot}65\ n + 1{\cdot}5$; the equilibrium constant K is equal to $a_{HC} \cdot a_U{}^m / a_A$ where a_{HC}, a_U, and a_A represent the respective activities of the hydrocarbon, the urea, and the adduct. The reciprocal of the equilibrium constant K is a measure of the stability of the adducts. The equations show that the stability increases rapidly with chain length. Actually, normal hexane is the first paraffin which can be adducted by urea at the ordinary conditions of temperature and pressure; the stability of the urea adducts of n-decane and higher homologues is such that they can be removed quantitatively. The stability of the complexes being directly a function of the chain length of the adductable component, a fractional adduction on the basis of the size of the molecules can also be achieved.[2, 9]

Equilibrium considerations indicate that the process of adduction should be carried out using solid urea or a saturate solution, at as low a temperature as possible. The decomposition of the complexes is obtained either by raising the temperature or by means of hot water or of a hot hydrocarbon solvent. The decomposition temperature, varying according to the stability of the complex, is lower than the melting point of urea (132·7° C) although a synthetic ceresin–urea complex stable up to 141° C has been reported.[14]

Potential applications of urea adduction in the petroleum industry are numerous; *i.e.*, in the manufacture of such products as low pour point aviation jet fuels, gas oils, and lubricating oils with, as by-products, n-paraffins suitable for further processing, such as by oxidation, and of speciality products, such as pure α-olefins. At present the main use of urea adduction is the application to the dewaxing of petroleum fractions without using external refrigeration in order to lower cloud points and pour points. Several commercial units are in operation.[3] The first commercial unit applying urea dewaxing went in operation in 1950 in L. Sonneborn's Petrolia, Pennsylvania, refinery.[15] The unit is designed for the improvement of the cloud point and pour point of medicinal white oils. Following the sulphuric acid treatment, the dewaxing process removes 3–4 per cent of straight-chain hydrocarbons from the oil, lowering the pour point from 25° to 0° F and the cloud point from 40° to 6°–8° F. The Deutsche Erdöl AG plant [16, 17] at Heide, of a capacity of 50 tons/day (340 bd) went on stream in 1954. Urea adduction is applied to the dewaxing of gas oils and spindle oils. Standard Oil Company (Indiana) has operated since 1956 the largest urea dewaxing plant designed so far,[18] and it has a capacity of 650 bd. The process is adapted to light lubricating stocks used for low-cold-test oils. In Russia the Moscow oil refinery [19] has put in operation a urea dewaxing process for the production of diesel fuels of −30° to −75° F pour point; the recovered low melting paraffins are suitable for fatty acid manufacture.

LABORATORY EXPERIMENTS IN UREA DEWAXING OF A WAX DISTILLATE

A Middle East wax distillate 255°–550° C suitable for the production of lubricating oils has been submitted to urea dewaxing under operating conditions such as might be applied easily on a large scale. Since the two steps involved in the process, formation of the urea n-paraffin adduct and its destruction for the recovery of urea and wax, are not independent, operating conditions must be determined taking both of them into consideration simultaneously.

Concentration of the Processing Products

The oil concentration in the medium is determined by the physical properties and *n*-paraffin content of the oil. Because of the oil viscosity, good contact between oil and urea is not achieved and difficulties are encountered during filtration. It is necessary to use a solvent to avoid these troubles. This solvent must dissolve oil and wax but not the urea. Toluene

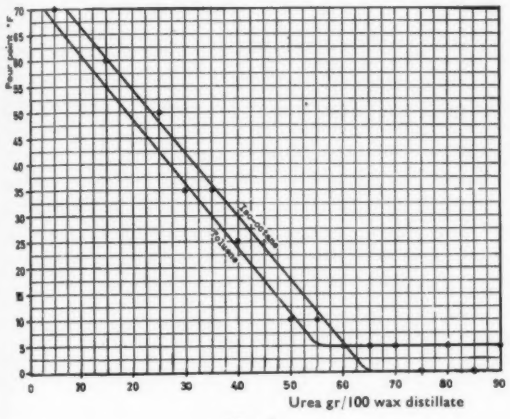

FIG 1

DEWAXING, WITH INCREASING AMOUNTS OF UREA, 100 G OF WAX DISTILLATE. UREA RECRYSTALLIZED FROM WATER, *iso*-OCTANE OR TOLUENE USED FOR DILUTION AND WASHING

was used. A 1 : 1 dilution permits good rates of agitation. The same solvent is used to wash the mother liquor from the adduct.

TABLE I

Influence of the Activator Concentration

Conditions: 100 g of wax distillate; urea crystallized from water; two hours agitation; filtration after 16 hours; solvent: *iso*-octane; room temperature.

Urea, g	Methanol, ml	Solvent, ml	% *n*-paraffins extracted	Congealing pt of *n*-paraffins extracts, ° F	Pour pt dewaxed oil, ° F
65	20	100	14·2	115	+ 5
65	10	100	15·0	115	+ 5
65	5	100	14·8	115	+ 5
75	5	100	14·3	115	+ 5
75	2	100	13·7	115	+ 5
75	1	100	14·3	115	+10
75	0	100	0	—	+75
75	5	150	14·8	115	+ 5
75	2	150	14·3	115	+ 5
75	1	150	11·9	118	+20
75	2 ml H_2O	150	0	—	+75

The urea concentration is fixed by the *n*-paraffin content. Above the theoretical amount of 3·5 times the weight of *n*-paraffins there is no improvement in the pour point of the dewaxed oil. Below the theoretical amount the pour point reduction is proportional to the weight of urea (Fig 1).

Methanol was used as the activator. The reaction is complete with as little as 3 ml of methanol for 100 g urea, although higher quantities can be used without detrimental consequences. Water alone in small amounts does not act as an activator (Table I).

References to the use of aqueous urea are often found in the literature. Treatments with aqueous urea were avoided here because mixtures of hydrocarbons and an aqueous phase are difficult to separate, and also because of the corrosion activity of aqueous urea. It appears also that the presence of water in urea has a detrimental effect on the pour point of the dewaxed oil (Fig 2). The influence of traces of water on the contact time is important too.

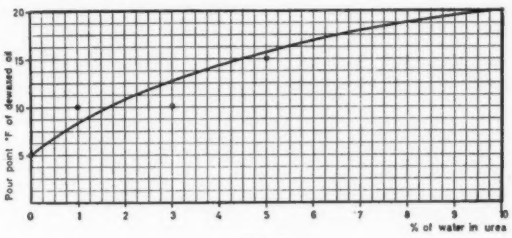

FIG 2

INFLUENCE OF PRESENCE OF WATER WITH UREA ON THE EFFICIENCY OF DEWAXING

Contact Time

For the application to a continuous process it is necessary that the contract times be as short as possible. Using urea recrystallized from water, the minimum pour point of the dewaxed oil is obtained only after 18 hours. If the urea used has been recovered from the adduct by treatment with hot toluene (100° C), a dewaxed oil with a similar pour point (+ 5° F) is obtained in only 30 minutes (Tables II and III; Fig 3).

TABLE II

Influence of Contact Time using Urea Crystallized from Water

Conditions: 100 g of wax distillate; activator: 5 ml methanol; solvent: 100 ml toluene; powerful agitation; 65 g of urea; room temperature.

Contact time, min	% *n*-paraffins extracted	Congealing pt of *n*-paraffins extracts, ° F	Pour pt of dewaxed oil, ° F
5	6·7	120	+60
15	9·5	118	+40
30	10·8	118	+30
60	11·6	118	+20
90	12·3	118	+15
120	13·6	117	+15
120 + 16 hr	14·5	115	+ 5
120 + 64 hr	15·1	115	+ 5

These results emphasize the importance of the urea regeneration step on the formation of the adduct. It is thus shown clearly that water should be excluded during all the phases of the process. The advantages

TABLE III

Influence of Contact Time using Urea Recovered from the Adduct with Hot Toluene (100° C)

Same conditions as Table II.

Contact time, min	Pour pt of dewaxed oil, ° F
5	+60
15	+20
30	+ 5
60	+ 5
120	+ 5
120 + 16 hr	0

thus gained permit a simplification of the installation because contact times are shorter, filtrations are easier, and corrosion due to urea hydrolysis is avoided. Losses of urea, even under the bench-scale conditions,

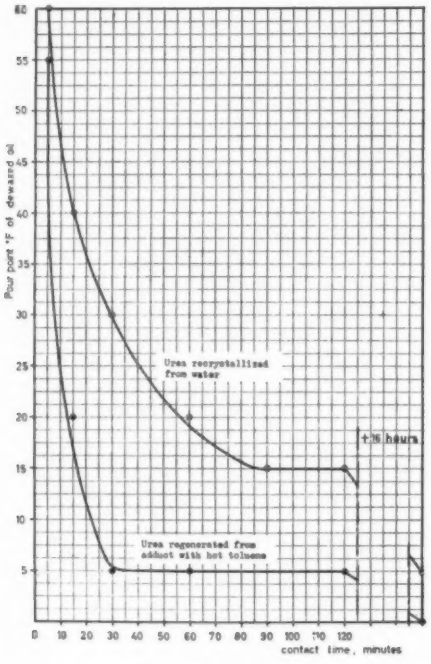
Pour point °F of dewaxed oil
contact time, minutes
Urea recrystallised from water
+16 hours
Urea regenerated from adduct with hot toluene

FIG 3

INFLUENCE OF CONTACT TIME AND TYPE OF UREA ON POUR POINT OF DEWAXED OIL

are very small—3 per cent after 8 cycles. The only drawback is the necessity of using large amounts of toluene with respect to the oil treated, approximately 500 per cent. In most of the pilot plant studies reported in the literature [3] and in the commercial process, the adduction and decomposition steps are made using urea in water solution. At Sonneborn's refinery,[15] although solid urea is used for the adduction step with methanol as activator, no solvent is used for the oil. Hot purified white oil is employed for separating wax from the urea adduct. A small amount of water is used to speed up the separation. It is stated in a patent [20] that in the absence of water urea becomes too finely divided and thus tends to clog the filter. This effect was not observed during the bench-scale investigations.

Influence of the Charge on the Efficiency of Dewaxing

Experiments were carried out using the whole wax distillate as a charge and the ten equal fractions obtained by distillation (Table IV). In the first case the efficiency was checked by examining the ten cuts obtained by distillation of the dewaxed oil. As the wax distillate is a large cut, distilling from 255° to 550° C, it is not surprising to observe different results according to the fraction treated: the viscosities of the

TABLE IV

Urea Dewaxing of Separate Fractions Obtained by Distillation

Untreated fractions			Dewaxed fractions					
Fraction number	Boiling pt of fraction, ° C at atmospheric pressure	Pour pt, ° F	Pour pt, ° F	Viscosity cS		vi	% n-paraffins extracted	Congealing pt of n-paraffins extracted ° F
				100° F	210° F			
1	255–355	+ 10	−75	4·42	1·49	—	16·8	liq.
2	355–388	+ 40	−60	10·10	2·41	53	17·0	84
3	388–393	+ 55	−45	16·16	3·16	43/44	18·5	95
4	393–405	+ 65	−30	23·96	3·97	42/43	17·1	102
5	405–442	+ 75	−25	34·36	4·88	52/53	19·3	108
6	442–460	+ 85	−15	46·35	5·78	60	19·1	113
7	460–470	+ 90	+ 5	72·0	7·37	57/58	19·4	122
8	470–483	+100	+15	115·0	9·96	57	14·8	129
9	483–512	+110	+30	175·8	12·73	60	13·4	136
10	512–550	+120	+50	306·8	18·16	63/64	8·3	151

TABLE V

Distillation of Whole Wax Distillate Treated with Optimum Urea—Pour Point 0° F

Fraction number	Boiling pt of fraction, ° C at atm press	Pour pt, ° F	Viscosity, cS		vi
			100° F	210° F	
1	255–345	−55	4·95	1·60	—
2	345–368	−45	12·03	2·69	52/53
3	368–388	−35	17·62	3·31	40/41
4	388–395	−25	25·27	4·14	49/50
5	395–405	−20	36·79	5·15	63/64
6	405–438	− 5	53·4	6·32	62/63
7	438–453	+ 5	82·1	7·95	57/58
8	453–475	0	132·4	10·43	53/54
9	475–498	+15	197·0	13·20	52/53
10	498–520	+25	337·7	18·75	57/58

component fractions vary greatly and the *n*-paraffin content is not the same throughout the whole cut. Tables IV to VI give the results for the different treatments.

The following conclusions may be drawn: light fractions, up to about 50 per cent of the charge, can be dewaxed efficiently by urea adduction; pour points lower than −10° to 0° F cannot be obtained for the higher fractions; better results are obtained when each fraction is treated separately than when the whole distillate is treated with optimum urea, except for the last fractions; the slope of the curves indicates that the heaviest *n*-paraffins are extracted preferentially when treating with deficient urea.

TABLE VI

Distillation of Wax Distillate Treated with 35 per cent of Optimum Urea, Pour Point + 25° F

Fraction	Boiling pt of fraction, ° C at atmospheric pressure	Pour pt, ° F	Viscosity, cS		vi
			100° F	210° F	
1	255–345	−25	4·78	1·57	—
2	345–380	− 5	10·75	2·41	27
3	380–395	− 0	16·64	3·30	60/61
4	395–415	+10	24·13	4·03	49
5	415–435	+15	32·78	4·85	64
6	435–448	+20	49·13	6·15	71
7	448–465	+20	78·0	7·71	57/58
8	465–490	+30	120·1	10·12	61/62
9	490–515	+35	185·4	13·17	60
10	515–550	+40	331·7	19·05	63/64

Comparison with Solvent Dewaxing

The results of the treatment of the whole wax distillate with methyl*iso*butylketone at −10° F are given in Table VII, and are represented in Fig 4. The

TABLE VII

Methylisobutylketone Dewaxing of Wax Distillate at −10° F

Fraction number	Boiling pt of fraction, ° C at atmospheric pressure	Pour pt, ° F	Viscosity, cS		vi
			100° F	210° F	
1	255–345	− 5	4·61	1·56	—
2	345–366	0	9·29	2·34	64/65
3	366–396	− 5	15·55	3·16	57/58
4	396–415	− 5	22·66	3·94	57/58
5	415–422	−10	29·93	4·62	61/62
6	422–443	−10	46·55	5·86	64/65
7	443–470	−15	80·1	7·78	55/56
8	470–448	−15	119·1	9·81	54/55
9	488–515	−10	209·9	13·51	48/49
10	515–550	− 5	409·5	20·54	53/54

examination of the distillation fractions obtained by dewaxing the wax distillate at approximately the same pour point (respectively 0° F and −10° F for urea and solvent treatments) shows that the efficiency of solvent treatment is constant throughout the whole cut and higher than urea dewaxing for the heavier fractions. For the lighter fractions, though, urea dewaxing is much more efficient; in order to reach the very low pour points obtained by urea dewaxing the solvent dewaxing should be conducted at much lower temperatures. The results suggest the use of urea dewaxing as a complementary method to solvent treatment. A laboratory study [21] of the dewaxing by both methods of a washed blue oil, suitable for making lubricating oils, leads to similar conclusions.

The poor efficiency of urea in dewaxing the heavier fractions is not surprising, since in waxes branched-chain paraffins predominate over *n*-paraffins at high molecular weights. A mass spectrometric study [22] of different waxes indicates the respective proportions of both types of paraffins on the basis of the molecular weight and confirms this point of view.

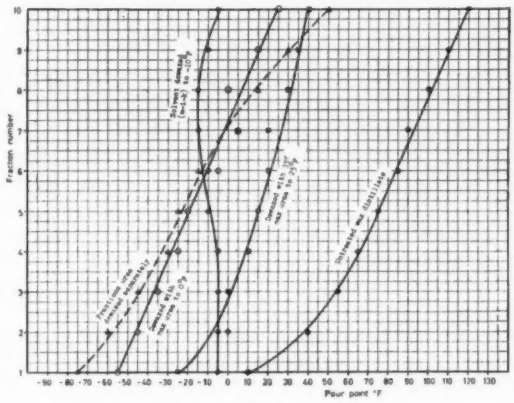

FIG 4

BENCH SCALE PREPARATION OF SOLVENT NEUTRAL LUBRICATING OILS

As already shown, urea dewaxing is particularly efficient for dewaxing the lighter fractions of a wax distillate and is poorer than solvent dewaxing for the heavier fractions. In order to obtain good results for all the fractions it seems worthwhile to combine solvent and urea dewaxing. Moreover, the preparation of solvent neutral oils requires first a solvent refining. The Middle East wax distillate chosen as lubricating oil stock was solvent refined with phenol. It was treated three times by 150 per cent by weight of phenol; in each treatment the phenol and oil were stirred at 155° F for 30 minutes and the mixture allowed to settle at 140° F during 5 hours. The yield in refined oil was 45 per cent. From this solvent-treated oil, solvent neutral oils are obtainable without processing at temperatures lower than 50° F (10° C) by two different methods:

(a) by a conventional solvent dewaxing at 50° F —a level interesting from an economic point of view—followed by urea dewaxing;

(b) by a simple urea dewaxing combined with the addition of a pour point depressant.

Successive Solvent and Urea Dewaxing

After preliminary study of different solvents and solvent blends suitable for refining, a 50/50 acetone–methylethylketone blend was selected taking pour point and yield into account. The same blend is also convenient for precipitating, washing, and recrystallizing the paraffins. 2000 g of refined oil were treated at 50° F by 5000 ml of the blend and after 10 minutes crystallization the paraffins were filtered and washed with 6000 ml of the same solvent. The yields were 68 per cent refined oil and 32 per cent raw paraffins (30 per cent and 14·2 per cent with respect to the feedstock). The pour point of the oil was 50° F.

The refined oil was urea dewaxed, by batch processing; 200 g of oil, 80 g of urea; 10 ml of methanol and 100 ml of toluene were agitated for 2 hours and left for one night. The adduct was washed with 250 ml of toluene after filtration. Toluene was distilled off to obtain the oil and the adduct was decomposed with water for recovering the *n*-paraffins. The yields after this treatment were 73·5 per cent dewaxed oil and 26·5 per cent *n*-paraffins (22·1 per cent and 8·1 per cent with respect to the wax distillate). The pour point of the dewaxed oil was −5° F. The dewaxed oil was distilled in ten equal fractions, the characteristics of which are given in Table VIII.

TABLE VIII

Distillation of the Solvent Refined and Urea Dewaxed Oil

Fraction number	Boiling pt of fraction, °C at atmospheric pressure	Pour pt, °F	Viscosity, cS		vi
			100° F	210° F	
1	270–345	−40	5·04	1·69	—
2	345–395	−25	9·64	2·49	89/90
3	395–400	−20	13·73	3·11	93/94
4	400–415	−10	17·94	3·66	95/96
5	415–435	0	23·43	4·32	99/100
6	435–460	+ 5	31·25	5·09	97/98
7	460–470	+ 5	43·23	6·16	96/97
8	470–485	+10	61·5	7·64	92/93
9	485–512	+10	91·2	9·82	94·95
10	512–540	+15	166·6	14·27	89/90

TABLE IX

Solvent Neutral Oils Obtained from a Wax Distillate by Solvent Treatment and Urea Dewaxing

Type of oil	Fractions blended	Pour pt	Viscosity, cS		vi	Flash pt, Cleveland, °F	Fire pt, Cleveland, °F
			100° F	210° F			
75 SN	2 + 3 + 4	−20	13·20	3·03	92	370	403
100 SN	5	0	23·43	4·32	99/100	421	453
200 SN	6 + 7 + 8	5	43·23	6·18	97/98	464	510
500 SN	9 + 10	10	115·3	11·36	92	536	568

The first fraction, considered as a heavy gas oil, was discarded; this lowers the oil yield to 20 per cent with respect to the starting wax distillate. The other fractions were blended in order to obtain 75, 100, 200, and 500 solvent neutral oils. The oil characteristics are given in Table IX.

Table IX shows that the characteristics can be considered as satisfactory. The viscosity indexes seem slightly too low and this is probably due to the solvent refining operation, as practised on a laboratory scale, being less efficient than might be expected from a countercurrent process applied in refinery operations.

Simple Urea Dewaxing Combined with the Use of a Pour Point Depressant

The phenol refined oil was dewaxed by urea adduction alone, according to the process described above. The dewaxed oil was obtained with a yield of 63 per cent (28·2 per cent with respect to the starting wax distillate); its pour point was +20° F. The characteristics of the ten equal fractions obtained by distillation are given in Table X.

TABLE X

Distillation of the Urea Dewaxed Oil

Fraction number	Boiling pt of fraction, °C at atmospheric pressure	Pour pt °F	Viscosity, cS		vi
			100° F	210° F	
1	270–365	−40	5·84	1·83	—
2	365–400	−30	11·50	2·77	88/89
3	400–415	−20	16·41	3·48	97/98
4	415–425	− 5	21·38	4·14	105/106
5	425–442	0	28·53	4·88	103
6	442–458	15	39·3	5·90	101/102
7	458–475	25	52·6	7·09	101
8	475–493	30	67·6	8·34	101
9	493–515	40	89·8	10·19	102
10	515–545	50	131·9	13·17	102

As in the other method, the first fraction, regarded as heavy gas oil, was discarded; in these conditions, the yield with respect to the starting wax distillate becomes 25·4 per cent. The other fractions were blended in order to obtain 75, 100, 200, and 500 solvent neutral oils. A commercial pour point depressant (type: naphthalene alkylated with a long-chain hydrocarbon) was added to the blends. The characteristics of the blended oils and the influence of a 1 per cent addition of the pour point depressant are given in Table XI.

The results given in Table XI show that the oils obtained by simple urea adduction and addition of a pour point depressant are of better quality than the oils obtained by a combination of conventional and urea dewaxing. Not only is the final yield better, 25·4 per cent against 20 per cent, but the viscosity indexes are also better by the second method. Furthermore, it is seen that the addition of a pour point depressant is strictly necessary only for the 500 SN oil; the other types might be acceptable as such or at least with addition of less than 1 per cent as shown. It

appears that, practically, lubricating oils of higher viscosities than the spindle oils can be obtained by simple urea dewaxing, without use of conventional

TABLE XI

Solvent Neutral Oils Obtained from a Wax Distillate by Simple Urea Dewaxing and Addition of a Pour Point Depressant

Type of oil	Fractions blended	Pour pt, ° F		Viscosity, cS		vi
		Without depressant	With 1% depressant	100° F	210° F	
75 SN	2 + 3	−25	−45	13·91	3·17	100
100 SN	4	− 5	−45	22·12	4·24	107/108
200 SN	5 + 6 + 7	10	−30	39·55	5·99	105
500 SN	8 + 9 + 10	40	5	43·07	10·41	101/102

solvent dewaxing. This point of view is confirmed by several recent papers published in Russia.[24-26]

SELECTIVITY DUE TO TREATMENT WITH DEFICIENT UREA AND APPLICATION TO THE POUR POINT LOWERING OF GAS OILS

Selectivity Due to Treatment with Deficient Urea

When *n*-paraffins of different molecular weights are present in a mixture submitted to urea adduction, a selectivity should be achieved as indicated by considering the stability of the adducts, provided of course that an appropriate method is employed. Zimmer-

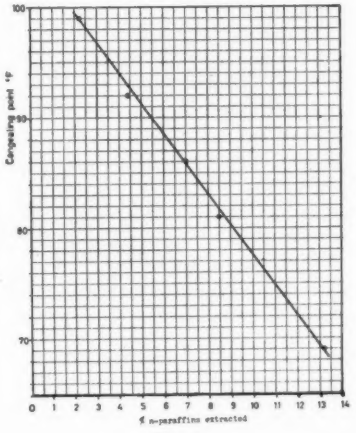

FIG 5

CONGEALING POINTS OF *n*-PARAFFINS EXTRACT OBTAINED BY DEWAXING A HEAVY GAS OIL WITH DEFICIENT UREA

schied *et al* [9] report a partial fractionation of *n*-paraffins by molecular weight in treating a waxy cut with deficient urea. By dewaxing various petroleum fractions with deficient urea it is found that the congealing point of the *n*-paraffin extracts is higher than when optimum urea is used. It is found also that the congealing point of the extracts is inversely proportional to the amount of urea used for dewaxing.

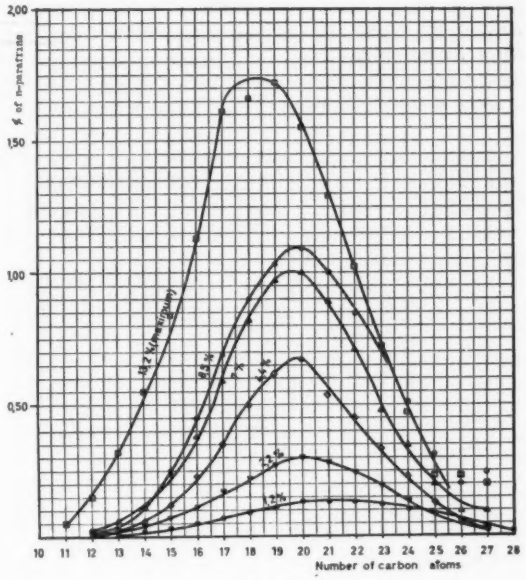

FIG 6

MOLECULAR WEIGHT DISTRIBUTION OF *n*-PARAFFINS EXTRACTED BY DEWAXING A HEAVY GAS OIL WITH DEFICIENT UREA

Weight per cent of *n*-paraffins shown on the curves.

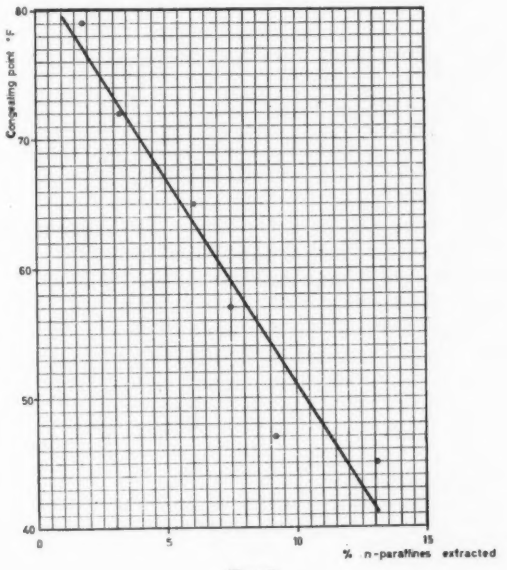

FIG 7

CONGEALING POINTS OF *n*-PARAFFIN EXTRACTS OBTAINED BY DEWAXING A LIGHT GAS OIL WITH DEFICIENT UREA

Fig 5 shows the congealing points of the *n*-paraffin extracts from a heavy gas oil.

This observation suggests that the heaviest normal paraffins are preferentially extracted when deficient

urea is used. This selectivity is clearly demonstrated by a gas chromatographic study. The partition by molecular weight in the extracts obtained by treating the same heavy gas oil with different amounts of urea is shown in Fig 6. Figs 7 and 8 represent respectively the congealing points and the gas chromatographic analysis of the *n*-paraffins extracted from a light gas oil.

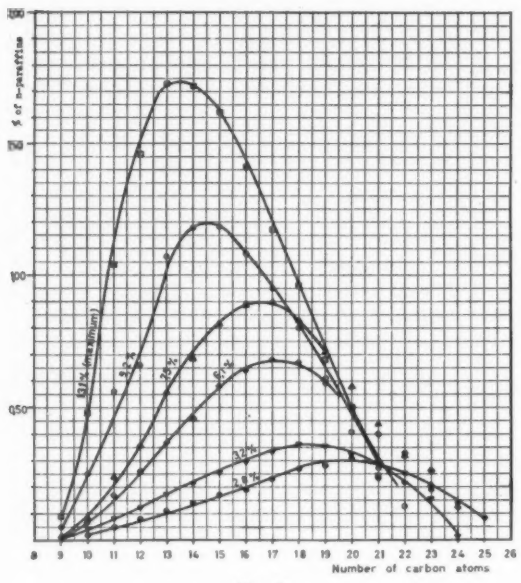

FIG 8

MOLECULAR WEIGHT DISTRIBUTION OF *n*-PARAFFIN EXTRACTED BY DEWAXING A LIGHT GAS OIL WITH DEFICIENT UREA

Weight per cent of *n*-paraffins is shown on the curves.

The comparison between Figs 6 and 8 shows that the effect of selectivity is more apparent for a light gas oil than for a heavy gas oil. This results from the difference in the stability of the adducts.

The gas chromatographic analyses were carried out with a commercial apparatus (Griffin and George Mk II). The column, one metre long, was filled with 25 per cent Dow High Vacuum Silicone Grease on Sterchamol. The temperature was 225° C. Hydrogen was used as carrier gas. The pressure was atmospheric at the inlet of the column and 200 mm Hg at the outlet. The peak areas, determined by multiplying peak heights and retention times, were assimilated to weight percentages. The analysis of a synthetic blend showed that this procedure gives a good approximation.

Pour Point Lowering of Gas Oils by Urea Dewaxing using Two Different Methods

Urea dewaxing is shown to be a very efficient process for the production of gas oils of very low pour point. For instance, the pour point of a diesel fuel dropped from 0° F to less than −70° F after treatment for maximum paraffin removal and 25 per cent *n*-paraffins were extracted, having a congealing point of +40° F.

The selectivity in the removal of *n*-paraffins, observed by the congealing points and the gas chromatographic analysis, is of practical importance in the processing. Indeed, there are two possibilities to produce a given pour point gas oil:

(1) The complete dewaxing of a portion followed by the blending with the untreated portion;
(2) the partial dewaxing of the whole charge.

The first alternative seems more profitable initially, the processing of a large amount of material being avoided. The second one should be better, as suggested by the selectivity in the removal: the same pour point should be obtained using a smaller amount of urea, since the heaviest molecule will be removed first, a fractional extraction being achieved. The results obtained by both methods are given in Table XII and shown in Fig 9.

It is thus shown that in order to obtain the same pour point it is necessary to remove more *n*-paraffins and thus engage larger amounts of urea when a dewaxed fraction is mixed to the untreated fraction. For instance, a pour point of −20° F is obtained by

TABLE XII

Pour Point Lowering by Blending

Per cent refined gas oil in the mixture	0	5	10	15	20	25	50	65	85	100
n-Paraffins extracted, %	0	1·25	2·5	3·75	5	6·25	12·5	16·25	21·25	25
Weight of urea, g	—	4·4	9	13	17·5	22	44	58	74	88
Pour point, ° F	0	0	0	−5	−5	−10	−20	−30	−55	<−75

Pour Point Lowering using Deficient Urea

n-Paraffins extracted, %	0	2·3	4·8	7·5	10	15	25
Weight of urea, g	—	8	17	26	35	52	88
Pour point, ° F	0	−10	−15	−25	−30	−55	<−75

treating 50 per cent of the gas oil with 44 g of urea and with only 19 g when treating the whole gas oil with deficient urea.

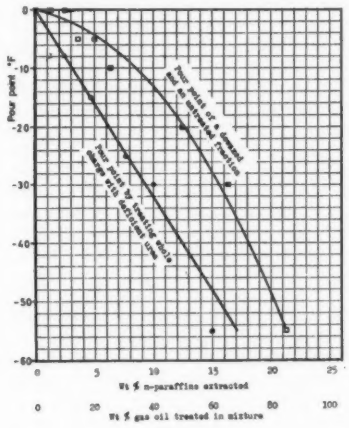

FIG 9

UREA DEWAXING OF A LIGHT GAS OIL

The application of the principle of selectivity obtained in dewaxing with a deficiency in urea has not to the authors' knowledge been reported in the literature.

ACKNOWLEDGMENTS

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DISCUSSION

L. N. Goldsbrough: I should like to compliment the authors on putting in their paper a great deal of interesting quantitative data. In fact, these data are so very comprehensive that I find it very difficult to find an opening for discussion, particularly on results of the dewaxing. I should point out, also, that I am at rather a disadvantage here, perhaps, in that the Shell Group of companies have been very interested in the urea extractive crystallization technique for many years, and qualitatively many of the effects which the authors describe are fairly familiar to me. This explains why I can accept almost all the quantitative data which the authors presented on dewaxing. I am also rather more of a process than a product man, and therefore many of my remarks will be directed to the process rather than the effect on products. In fact, I will introduce only one point on the product question at the moment.

The authors show that it is possible to use urea treatment alone for dewaxing, if a pour point depressant is used. I wonder if it is entirely fair to make such comparisons. Have the authors any information on the effect of pour point depressants on the products from conventional solvent dewaxing? I think it quite likely that the effects will be much less marked, but I would like to know whether the authors have confirmation of that.

There is, also, the effect on vi as well as pour point, and I would be interested to know what significance the authors attach to that. But it seems to me that if the effect of pour point depressants is the same both on urea dewaxed and conventionally dewaxed material, then the justification for using them is perhaps economic rather than technical.

Coming on to the question of the process which the authors have outlined, to develop a urea extractive crystallization process requires that one should solve three problems. First, the contacting of the hydrocarbon and the urea; secondly, the filtration of the adduct and the removal of non-adducted oil from it; and thirdly, urea and solvent recovery problems.

I felt that the contact times which the authors quoted, except in the case of urea recovered by hot toluene decomposition of the adduct, were rather long, and I feel that perhaps they may not have selected the optimum combination of solvent and activator. The authors quote a paper in which a colloid mill was used to obtain effective contacting of the urea and hydrocarbon by purely mechanical means, in which it is shown that the

contact times can be very short. In common with many other workers, they have chosen to use methanol as an activator. Although this may be very much a point of detail, the authors mention that preferably the urea should not be soluble in the toluene. Surely, in order to obtain good contacting between the urea and the hydrocarbon, a certain amount of mutual solubility of the two in the solvent is necessary, and this, presumably, is where the activator plays its part. And I think this is borne out by the fact that the authors found out that water alone could not be used as an activator, and that when water was present it prolonged the reaction time, presumably, I would think, because it affected the mutual solubility relationships.

This question of the behaviour of urea recovered from the decomposition of the adduct with a hot solvent is very interesting. I have come across this sort of thing before, and the differences, as in the authors' case, have been quite striking. I wonder if the authors would care to comment on a rather wild suggestion, that when an adduct is decomposed in hot toluene in the complete absence of water the urea finds difficulty in reverting wholly to the tetragonal form, and stays in a rather unhappy hybrid state between the tetragonal and the hexagonal, and therefore can form the adducts more readily when re-contacted with the hydrocarbon. Alternatively, it is just possible that a small quantity of adduct may not be decomposed and, acting as a seed, may promote rapid reaction when the urea is next reacted with hydrocarbons.

On the question of filtration of the adduct, and the removal of any adhering non-adducted hydrocarbon, I should like to enquire whether the authors used fresh or recovered urea. That is not very clear from the paper, and I am interested because I have come across some information which suggests that the presence of small quantities of water (such as one finds in urea re-crystallized from water, or obtained from conventional sources) can have a significant effect on the filterability of the adducts. I wonder if the authors would care to state whether at any time they encountered difficulty in the filtration of the adduct or, for that matter, of the urea recovered from decomposition of the adduct with hot toluene.

The authors quote some data for re-cycling of urea, and, if I calculated this correctly, this worked out at about 6 or 7 lb of urea loss per ton of feed. We found, in some of our rather early economic assessments for large volume applications, that we could not tolerate anything like this rate of urea loss. The reason for this was that, in considering large volume applications, although one might obtain a substantially better product in some respects, one may not get much of a premium for it. And therefore the process as a whole must be as cheap to operate as any process which it replaces. On that score also, the amounts of solvent which the authors used seem quite high. I think they are 500 per cent of the total, and I am not sure entirely how those are distributed. I presume that something like 400 of the 500 per cent are used for solvent washing. I wonder whether that was a minimum figure, or a figure which the authors selected for convenience.

The point which I made about economics is, I think, borne out largely by the type of commercial application where the urea extractive crystallization process has been used. In general, I think it is true to say that only certain speciality products have been produced commercially and economically by urea treating. I wonder if the authors would care to take up this point, and to discuss what they think of the prospects for really large volume applications of this very interesting process.

I have two final comments. In the very interesting data about the selectivity of the urea process, the authors discuss the possibility of using the process with deficient urea to make diesel fuels with improved pour points. When one takes out paraffins, of course, one is also tending to reduce the cetane value. I wonder if the authors consider that a satisfactory compromise between cetane value and pour point can be achieved.

My final point deals with a piece of information which Dr Marechal introduced but which was not in the preprint, concerning the adduction of compounds which are not a wholly straight chain. If I recall the figures correctly, an adduct can be formed from an 8-carbon straight-chain compound, but that with a methyl or ethyl side chain present, the number of carbon atoms in the molecule rises to 14 and 24 respectively before equivalent adduction occurs. This surely is not generally true. If the side chain is very close to the end of the molecule I think that in many cases a certain amount of distortion of the urea hexagonal structure can be tolerated, so that in fact the minimum chain length of a compound with a small side chain which can be adducted is probably very dependent upon the position of that side chain.

Dr J. Marechal: I must point out right away that we are definitely at a disadvantage to Mr Goldsbrough in that we have unfortunately never carried out pilot-plant studies.

Concerning pour point depressant additives, I agree that it is unfair to present their effect in one case and not in the other. But our purpose was to show that it is possible to apply urea dewaxing alone to the preparation of conventional lubricating oils. For that reason we tried to improve the results as much as possible by using pour point depressants. We did not directly compare the action of these additives on oils obtained by conventional dewaxing, nor did we directly compare the viscosity indexes of the products obtained by the two dewaxing processes. I do not think there will be a large difference. Of course, the solvent, toluene, plays a role during the contacting step, and the presence of water has quite an influence on filterability. Let us look at what is known from the literature on commercial operations. It is not known if water is used in the Standard Oil of Indiana process; water is not used in Sonneborn's process, except that small amounts are added during the decomposition step, in order to speed up the decomposition; workers at Deutsche Erdöl claim that it is profitable to use a quantity of water between 10 and 40 per cent during the adduction step; this way they obtain the adduct in the form of spheres having a diameter of 10 mm.

During the adduction step, toluene acts physically in lowering the viscosity of the oil. We do not think that mutual solubility is an important requirement. The activator might perhaps play a role here, but it is more probable that its action is the freeing of the urea molecules from their tetragonal lattice by formation of hydrogen bonds between urea and methanol. The great activity of the urea obtained by decomposing the complex with hot toluene, in the absence of water, might be due to the formation of very small crystalline aggregates. It seems that after decomposition the urea returns to the tetragonal configuration. This has been shown in a Canadian paper we cite and is confirmed by the fact that after decomposition the hexagonal lattice collapses. As an indication it is not possible to use urea as such for another adduction, considering that the channels are preformed. We tried this and it did not succeed, although of course this is only a rough approximation. It is certainly possible that, because of incomplete

decomposition, traces of urea complexes might act as seed, thus promoting the high activity of urea. In the absence of water it is difficult to be certain that all the complexes are really decomposed.

The urea loss Mr Goldsbrough considers as high must be considered as a maximum; the figure was given as an indication. Here we are definitely at a disadvantage, since all the experiments were made on a bench scale and losses are of course higher in these conditions than in pilot-plant experiments.

The figure of 500 per cent of toluene is a maximum given for convenience; this amount includes the 100 per cent of solvent used for dilution of the wax distillate during the adduction step. A slightly larger amount is used for the decomposition itself; the total amount reported is high because it also includes a large amount of solvent used for washing, to make sure that the *n*-paraffins recovered are not contaminated by non-adductable material.

Regarding large volume applications, an examination of the literature does not give much of an answer. Workers at Standard Oil of Indiana claim that investments of a urea dewaxing plant to produce very low pour point products are of the same order as a solvent dewaxing unit to 0° F on the basis of 1000 bd; operating costs are similar. These costs should be much less for larger units. Deutsche Erdöl estimates that investments for an urea dewaxing unit are smaller, by a figure of 50 to 65 per cent; the operating costs are smaller too. But this is not too clear a picture. I prefer the comparison of Standard Oil of Indiana, on the basis of the capacity and the pour points. It should also be mentioned that Deutsche Erdöl claims that the urea process is more economical than solvent dewaxing when the *n*-paraffin content of the oil is lower than 15 per cent.

Anyway, it might be said that the urea adduction process could perhaps be more interesting for the preparation of relatively small quantities of speciality products. For instance, in Sonneborn it seems that the process is economically sound because the amounts treated are rather small, the capacity being about 200 bd, and also because it is not a continuous but a batch process, so that investments are much smaller.

Regarding applications of selectivity, we did not measure cetane numbers and evaluate diesel indexes, but I suppose that if we extract a smaller amount of *n*-paraffins by the deficient urea method, the diesel index of the dewaxed fuel will be better than if we extract a larger amount of *n*-paraffins by treating the whole charge in order to obtain a product having the same pour point.

I certainly agree with Mr Goldsbrough on his comment on the substituent groups present on straight chains. The figures shown were merely given as an indication in an attempt to justify the lack of activity of urea in the dewaxing of the high molecular weight fractions.

Dr P. de Radzitzky: Concerning the adduction of not wholly straight-chain paraffins, I must point out that on the figure shown by Dr Marechal the length of the straight chain was given for a substitution on the second carbon atom. Of course, if the methyl or ethyl group is located elsewhere, one needs respectively more than 14 or 24 carbon atoms in the straight chain in order to get an adduct with urea.

Concerning the use of water, we never used water in the adduction step, but most of the time we used it for the decomposition step. Consequently, the urea we used was generally recrystallized from water.

Nevertheless, we used for eight successive adduction cycles urea regenerated with hot toluene alone, without encountering any troubles during filtration.

Dr A. Winward: Considerable technical interest and continuous effort on continuous urea extraction as an *n*-paraffin separation process was generated by the original German disclosure of about 20 years ago. The possibilities of obtaining by this route pure *n*-paraffins as a keystone of petrochemical development, high grade kerosines up to 50 smoke point, diesel and jet fuels of improved low temperature performance, and also higher octane virgin naphthas are almost self-evident to the petroleum technologist.

However, while allowing that interest is still at a high level, despite the introduction of molecular sieves, which, as the authors point out, are more useful for extracting relatively short-chain paraffins, the important question arises—*why* has commercial exploitation of the urea process been so small?

It must be admitted that despite some reported developments in Russia, the extent of which I have no knowledge, the total Western World urea treating capacity, especially for fuels production, has grown at a very small rate compared with other refinery processes. Are the factors basically economic because of relative product values, or are process difficulties involved? In my view, the answer, at present, is that both factors probably contribute equally. I would like to comment on these briefly, in relation to middle distillate treating, as I think they have a special bearing on the paper presented.

First, with regard to basic economics, even on the assumption that one has a low cost process in terms of direct operating costs, overall profitability depends to a tremendous extent on the realization obtainable for by-product *n*-paraffin extracts, either pure and sulphur-free, or as waxy diluents. If "kerosine" or "white-spirit" value can be realized by this by-product, in general the process is demonstrably very attractive, but if the realization obtainable is not above, say, marine diesel fuel value, the incentive for the application of urea extraction may be only borderline.

Secondly, with regard to processibility, which of course affects the direct operating cost and investment required, it should be recognized that the main difficulties arise from the bulky nature of the urea complex. For example, a 10 per cent, weight to volume, urea treatment of middle distillates is equivalent to a settled bulk volume of urea complex of 50 to 60 per cent. The use of rotary filters for separation, publicized in the technical contributions of the Shell Company, must necessarily increase processing cost relative to a continuous process involving solid urea at all times—a process in which urea is continually cycled in the regenerated or complex form and efficiently washed with process streams to remove entrained liquid (non-adducting).

I have no doubt that there are still technological developments to be made which will improve this solid urea process, but published literature and our own data show that the concept is basically sound. Some effects are of particular importance.

(1) Solid urea can be continually regenerated provided there is adequate pH control. The question posed by the previous speaker on "hybrid" crystal formation, is, I think, shown by Fig A, which shows three forms of solid urea. The figure on the left (*a*) is fresh urea; (*b*) is a photograph of urea complexes; (*c*) is a photograph of regenerated urea after it had been in a cycle for eight times—the *n*-paraffins have been removed from that urea, and it can be seen that the solid looks more spongy than

the middle picture. It possibly shows also the hybrid structure which the previous speaker mentioned.

(2) Settling rates of solid urea complex can be increased many times by proper control of the dissolved water content of feedstocks; this is, of course, very important for the design of settling equipment. Incidentally, perhaps contrary to the authors' findings, we found no significant effect of water content, on reactivity, up to the water saturation point for the feedstock involved.

(3) Solid urea/middle distillate slurries up to 30 per cent weight to volume are pumpable under slight positive suction pressure.

(4) We found reaction times with regenerated urea to be very rapid indeed, in contrast to those presented in the paper. In our work even the regeneration times were considerably less than those mentioned. I wonder if this is perhaps due to use of the aromatic solvent used in the authors' work.

(5) For reactions in the presence of "deficient urea" (to use the authors' terminology) we found evidence of an optimum treating temperature yielding maximum cloud point or freezing point depression. Incidentally, as a good working rule, we found 1 per cent of *n*-paraffins rejected in a paraffinic middle distillate gives an approximate depression of 3° F in freezing point or cloud point. I think that this ties up well with the extensive data which the authors have presented.

E. Bowes: I must join the previous two speakers in congratulating the authors on a very interesting paper, especially to those of us who have done work on this subject. It is all the more valuable for being on one crude oil, but I would like to ask the authors if they have done work on similar fractions from different crude oils, and whether they have found quite different ultimate pour points.

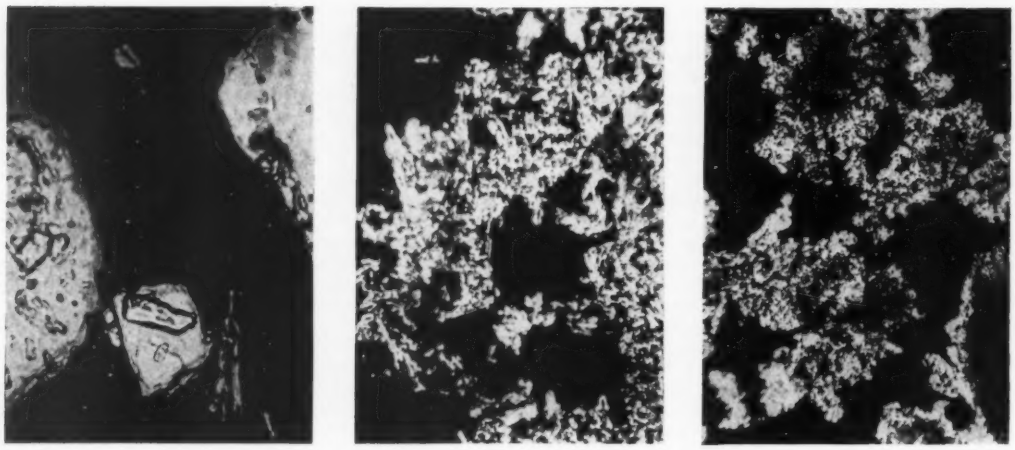
Dr P. de Radzitzky: We have only worked with Middle East distillates and do not have any experience with other crude oils.

R. A. Dean: I would like to ask if the authors have any data on the paraffin content of the adducts. We have found that with fractions boiling at 300° C there are *iso*-paraffins present, and I should have thought that with higher boiling fractions in the region of 500° C there would be an appreciable amount of non-*n*-paraffins present.

Another thing I wondered was whether the solvent used during the adduction affected the final cloud point at all. Fig 1 has a slightly lower pour point for the *iso*-octane solvent than for the toluene solvent.

The third point concerns the high boiling fractions from the waxy distillate that had a pour point of 40° C. I would like to know whether the hydrocarbons giving that pour point were *n*-paraffins that were not removed, or whether there was some other type of hydrocarbon.

Dr J. Marechal: We have no data on the *n*-paraffins content of the adduct; we did not investigate the nature of the *n*-paraffins by mass spectrometry.



(*a*) (*b*) (*c*)

FIG A

SOLID UREA REACTANTS

There is a slight influence of the solvent on the pour point of the dewaxed oil. We have no explanation for the difference between toluene and *iso*-octane, as shown in Fig 1.

Regarding the last fraction, the one having a pour point of 40° F, we suppose that the strictly *n*-paraffins were removed but that this fraction contains a relatively important amount of non-adductable paraffins having a linear structure but containing various substituents.

Dr P. de Radzitzky: We have an indication that they are in fact long-chain paraffins with a substituent, because such paraffins, when extracted by conventional solvent dewaxing, are more or less micro-crystalline paraffins, and such micro-crystalline paraffins are known as non-straight-chain paraffins.

It has been seen on the chromatogram that there were up to 28 carbon atoms in the *n*-paraffin, without any *iso*-paraffin. We can say that up to around 28 or 29 carbon atoms there is very little *iso*-paraffin adducted.

R. A. Dean: This is in contrast to what we have had on gas chromatography, where we have found *iso*-paraffins in urea adducts with 14 and 15 carbon atoms. They have shown up on the chromatogram very clearly.

Dr J. Marechal: I must say, with regard to this last comment, that the chromatogram shown on the slide was obtained in a relatively short time, but we have sometimes used a longer column, with the result that the chromatogram was obtained in much longer times, of the order of 8 hours. Even in these conditions, except in one case, we found only *n*-paraffins. But it is perhaps difficult to be sure on this point, because the presence of non-*n*-paraffins depends, I think, on the way in which one carries out the washing of the adduct. As these complexes formed with these non-*n*- but adductable paraffins are not stable at all, it might, after all, be possible that they are eliminated when washing the adduct.

R. A. Dean: I think the resolution we had on our GLC was probably better than yours. We obtained these peaks on columns of about 2000 plates. We have also examined them on capillary columns, where they show up much more plainly, of course.

E. Bowes: It seems a pity that such detailed and quantitative work should go under the guise of Middle East crude oil. I wonder if the authors would like to name the field from which the crude oil came.

Dr J. Marechal: Some of them were Kuwait and Iraq, some were 50–50 mixtures of them.

B. G. Post: In our laboratory we have worked on waxes and have been interested in this problem of urea selectivity. In a few experiments that we have conducted on urea adducts, using Linde 5A molecular sieves, we have never found a case, when applied to paraffin waxes, where one could obtain complete agreement between the amount of adduct formed and the amount of material taken out by a molecular sieve. If one takes the adduct, and then treats it with a molecular sieve, there is always a small amount of residue that does not sorb on the sieve. Whether this is due to the fact that the adduct is not completely washed, as the authors have indicated, or whether there is poor selectivity of the urea itself, is not known, but in none of our experiments did we ever obtain complete agreement.

Dr P. de Radzitzky: I think that when working in the absence of water it is much easier to completely wash the adduct, because there is only one liquid phase present. But when water and hydrocarbons are present together it is quite difficult to wash the adduct completely.

L. N. Goldsbrough: Is there some confusion here? There is a distinction to be drawn between the mere washing out of physically adsorbed, non-adducted hydrocarbons, and the decomposition of the less stable adducts during washing.

Dr J. Marechal: I believe it is strictly impossible to distinguish between both of them. As Mr Goldsbrough points out, some hydrocarbons might be physically adsorbed. If one washes too much, to make sure one removes them entirely one is probably going to destroy at the same time the less stable adducts formed with some *iso*-paraffins. How is it possible to distinguish between the two kinds?

L. N. Goldsbrough: If one has an *iso*-paraffin, with relatively minor side chains, it is probably quite strongly adducted, and I think that if that were decomposed during adduct washing, some *n*-paraffin will be lost as well by decomposition. A great deal depends on the conditions of washing.

The meeting then closed with a unanimous vote of thanks to the authors.

THE PHASE RELATIONS OF HYDROGEN–OIL SYSTEMS UNDER PRESSURE *

By S. R. C. DRYER † (Associate Fellow)

SUMMARY

The phase relationships of hydrogen–oil mixtures have been investigated using a continuous flow flash still. System conditions covered the range 150 to 1000 psig, 100° to 420° C, and 500 to 6000 SCF/B hydrogen–oil ratio. Gasoline, gas oil, crude oil, and residual feedstocks were used.

Experimental results indicate that hydrogen acts mainly as an inert which reduces the partial pressure of the oil components. As would be expected, increase in temperature or hydrogen–oil ratio, or decrease in pressure, all favour increased vaporization.

On the basis of experimental results a method of calculation has been developed which can be applied to many petroleum fractions. The method of calculation is a normal rigorous one, but the hydrocarbon equilibrium vaporization constants used are derived from normal vapour pressure charts. Empirical corrections for different types of fractions increase the precision of calculation.

INTRODUCTION

During the last twenty years there has been an increase in the use of catalytic refining processes in which hydrogen takes an active part. In the development of such processes, especially in the unit design stage, knowledge of the phase relationships existing in various parts of the unit is necessary. For example, in the design of heat exchangers the amount of oil entering and leaving the exchanger in the vapour phase must be known so that the necessary area for condensation can be calculated. Using well-established methods, phase relationships can be calculated generally for systems containing hydrocarbons alone, but the presence of hydrogen in significant amounts gives rise to erroneous results. Published experimental data on hydrogen–oil systems are very sparse and confined mainly to systems containing low-boiling hydrocarbons at temperatures of less than 150° C. As most of the present hydro-refining processes operate at temperatures above 300° C with feedstocks boiling above 100° C, published information is of little use for developing a suitable method of calculation. The work described below was therefore done with the main aim of providing experimental data for specific process calculations, the secondary aim being to establish, if possible, a method of calculation which would be suitable for application to hydro-refining process calculations in general. Neither the experimental work nor the method of calculation needed to be extremely precise in view of the accuracy of data to be used in conjunction with them; a precision of less than 10 per cent in oil vaporization values was therefore considered to be satisfactory for this type of work.

Up to 1950, investigations of the phase relationships of hydrocarbons were done in a modified form of the classical Andrews apparatus.[1] The hydrocarbon sample was confined over mercury in a silica barometer tube, pressure being applied to the sample by a hand-operated ram in the mercury system, and heat by sliding an oven over the length of tube occupied by the sample. The amount of sample remaining in the liquid phase could be observed visually and measured by cathetometer. Using this apparatus for hydrogen–oil mixtures, it soon became apparent that it suffered from two serious disadvantages:

(1) As the sample was static, thermal degradation occurred if the system temperature remained above 300° C for any length of time; this change in composition affected phase relationships and also the experimental life of the sample was appreciably reduced.

(2) At high hydrogen–oil ratios the volume occupied by oil in the liquid phase was extremely small and hence difficult to measure accurately; in extreme cases the errors in measurement were of the same order as the liquid phase volume.

Because of these disadvantages and also the anticipated demand for experimental data on hydrogen–oil mixtures, it was decided to design and erect a unit which did not suffer from these disadvantages and which would be flexible enough to operate over a wide range of operating conditions and feedstocks. The basis chosen for design was a continuous flow unit in which hydrogen and oil would be mixed and fed into a small flash chamber capable of operating at temperatures up to 500° C and pressures up to 1000 psig. After attaining equilibrium the two phases would be removed from the high-temperature zone as quickly as possible and metered accurately.

* MS received 17 September 1959.

† The British Petroleum Co. Ltd.

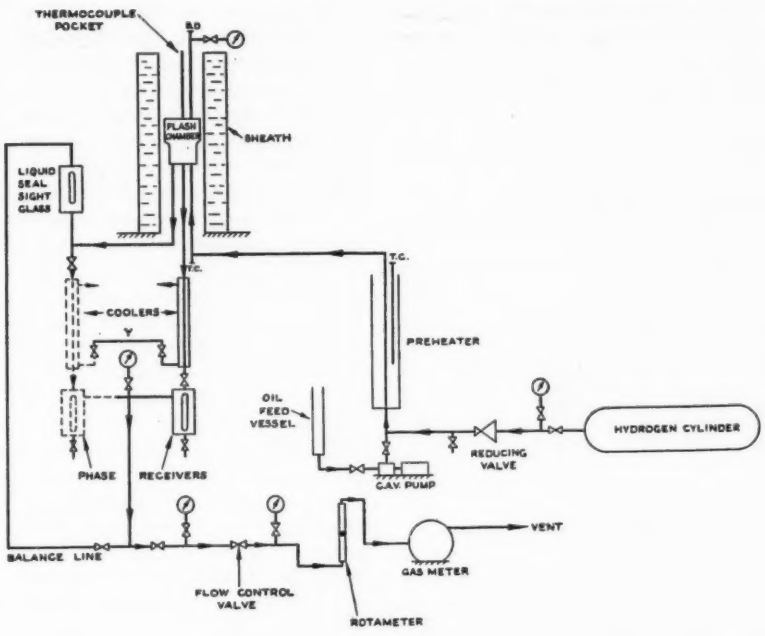


FIG 1

HIGH PRESSURE FLASH STILL—FLOW DIAGRAM

DESCRIPTION OF UNIT

Fig 1 presents the flow diagram of the unit and Fig 2 shows the actual layout.

A high-pressure hydrogen cylinder manifold located outside the laboratory supplies pressure to the unit through an emergency shut-off valve and a reducing valve installed on the unit. The reducing valve maintains a constant downstream pressure by the automatic operation of a spring-loaded diaphragm. A hand-set needle valve controls hydrogen flow and reduces exit gas pressure to near-atmospheric for metering by rotameter and gas-meter. A variable positive-displacement pump injects oil from a calibrated vessel into the hydrogen stream immediately before the preheater.

The preheater consists of two concentric sections of pipe containing molten lead in the annular space. Heat input to the lead bath is controlled manually on an auto-transformer connected across windings on the outer section of pipe. The preheated stream then passes through an electrically-heated transfer line and enters a constant-temperature zone which extends for one foot above and two feet below the flash chamber. The constant temperature is achieved by enclosing the flash chamber and all inlet and outlet lines in an insulated sheath heated on the inner wall by four electrical windings each connected to an auto-transformer. Seven surface thermocouples indicate sheath temperatures, and pocket thermocouples in

FIG 2

HIGH PRESSURE FLASH STILL

the preheater outlet, transfer line outlet, and flash chamber transmit temperatures which are continuously recorded.

Three requirements influenced the design of the flash chamber:

(1) Constant temperature throughout the chamber.
(2) Complete phase separation.
(3) Minimum liquid phase residence time.

The details of the flash chamber are shown in Fig 3.

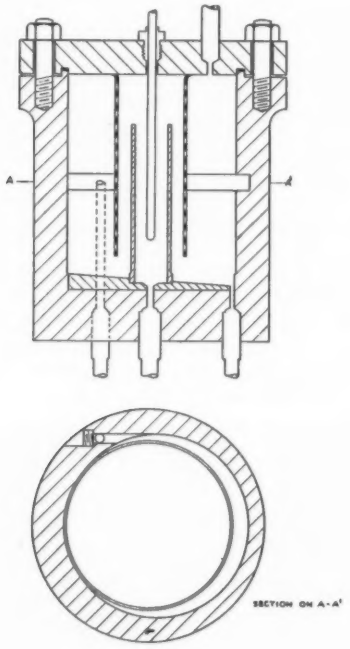


FIG 3

HIGH PRESSURE FLASH STILL—CONSTRUCTIONAL DETAILS OF FLASH CHAMBER

Massive construction of the flash chamber provides a heat reservoir round the flash zone and reduces any effects from excessive variations in sheath temperature. In addition, the inlet stream passes into the flash zone through a channel in the flash chamber body, thus reducing variations in feed temperature. This inlet stream enters the flash zone in a horizontal plane, reducing any entrainment tendencies due to vertical velocities. Moreover, the inlet stream enters tangentially into a groove cut in the flash chamber body, and full use is made of centrifugal force to throw the liquid phase droplets on to the chamber walls. A mesh cylinder surrounds the vapour phase outlet and reduces further the possibility of entrainment. Finally, the use of an inclined base to the flash chamber ensures that liquid phase drains from the flash zone as quickly as possible.

On leaving the flash chamber, the liquid phase passes through a U-tube into a sight-glass about one foot above the base of the adiabatic sheath. Thus a liquid level always exists in the high-temperature section of the liquid phase outlet line and prevents vapour phase by-passing or condensing in the liquid phase leg. A hand control valve at the base of the sight glass keeps this liquid seal intact and allows liquid phase to flow constantly into the cooler and thence to the liquid phase receiver.

On leaving the flash chamber, the vapour phase passes directly to a condenser where the oil present in the vapour phase is condensed. The stream of oil and hydrogen flows into the vapour phase receiver where the oil is separated. The hydrogen passes on to the rate control valve, metering equipment, and vent.

The above description applies when the feedstock gives products which can be easily handled at ambient temperatures. With gasoline feedstocks a low temperature coolant circulates through the "vapour-phase" condenser to prevent loss of light ends in the hydrogen stream. With crude oil and residual feedstocks the liquid phase is generally too viscous to be free-flowing at ambient temperatures. Then the liquid phase cooler is removed and a small electrical winding installed on the liquid phase outlet line and sight glass. The warm residue can then run directly from the base of the sight glass through the hand-control valve. In the case of residual feedstocks a further winding on the feed vessel and pump eases pumping problems.

The complete unit is very compact and occupies a floor area of 18 square feet. The only services required are electricity and cooling water, the low-temperature coolant being supplied by a portable pump and cooler when necessary. The unit operates in normal working hours with occasional overnight adjustment of preheater and adiabatic sheath temperatures. One experimental determination consists of a run-up period of about four hours followed by two or three hourly tests in which accurate operating conditions and weight balances are recorded. All liquid streams are weighed in and out of the unit by running to set levels. Phase relations are recorded as a vaporization value, which is the weight percentage of the liquid feedstock vaporized. The following data indicate the steadiness of operation during the commissioning period of sixteen test runs:

Temperature .	$\pm 1°$ C
Pressure . .	$\pm 0{\cdot}5$ per cent gauge reading
Hydrogen–oil ratio	$\pm 1{\cdot}6$ per cent arithmetic mean variation

EXPERIMENTAL WORK

In order to test the apparatus, two series of runs were done in which temperature, pressure, and hydrogen–oil ratio were kept constant for each series,

the feed rate only being varied. This would cause a change in vapour velocity which should be sufficient to effect materially any entrainment that existed, and hence the vaporization values. The operating conditions chosen for each series ensured that vapour densities varied, vaporization being high in one case and low in the other. A normal gas oil of Middle East origin was used as feedstock throughout. The results obtained are summarized in Table I.

TABLE I

Verification of Equilibrium Flash Conditions

Pressure, psig	200			200		
Temperature, °C	420			381		
Hydrogen–oil ratio, SCF/B	300			270		
Oil feed rate, ml/hr	541	978	1477	612	982	1410
Gas oil vaporization, % wt						
Hourly	86·3, 91·7	85·0, 90·6	87·1, 88·0	38·5, 40·0	35·6, 35·0	36·8, 36·9
Mean	89·0	87·8	87·5	39·3	35·3	36·9

These results show that no consistent trend of change in vaporization values occurs in either of the series of runs. If entrainment does occur, its effect falls within the variations of operation and cannot be detected. The mean vaporization values indicate a tendency towards higher vaporization at low oil feed rates, presumably due to the longer residence time in the flash zone, but this tendency is not consistent at the higher feed rates. As all further experimental runs used feed rates of less than 500 ml/hr, it is reasonable to assume that entrainment is negligible under normal operating conditions.

On the basis of this assumption the variation in experimental data can be assessed from the above results. Hourly vaporization values have a maximum variation of 5·6 and an arithmetic mean variation of 2·3. Some of this variation can be attributed to lack of operating experience as the arithmetic mean hourly variations for subsequent runs on various feedstocks were:

(1) 1·9 for forty runs on gas oils.

(2) 1·1 for twenty runs on crude oil and residues.

(3) 0·8 for twenty runs on gasolines.

On the basis of the hourly variations for these subsequent runs, a short term repeatability has been calculated. In each run hourly vaporization values were obtained, the mean of two such values being taken as the published value. From these hourly vaporization values, a short term repeatability can be calculated for hourly vaporization values, using the expression:

$$R = \sqrt{2}\, t_n \sqrt{\frac{\Sigma d^2}{2N}}$$

where R = short term repeatability * (95 per cent probability limits);

t_n = " Student's t " for N degrees of freedom;

d = Difference between each pair of hourly vaporization values;

N = Number of pairs of hourly vaporization values.

Table II presents the short term repeatabilities for the three types of feedstocks used.

TABLE II

Short Term Repeatability of Experimental Data

Feedstock type	Short term repeatability of hourly vaporization values
Gas oil	5·0
Gasoline	2·1
Crude oil and residue	2·1

No opportunity has arisen to determine repeatabilities for mean vaporization values. However, it is reasonable to assume that they will approximate to the above values and possibly be lower.

Previous work on phase relationships had only been done on a modified Andrews apparatus with gas oil and crude oil feedstocks. Experimental data were obtained therefore on the flash still under operating conditions similar to some of this previous work. The correlations obtained are summarized in Table III.

TABLE III

Correlation with Modified Andrews Apparatus

Feedstock	Gas oil			Crude oil
Operating Conditions				
Pressure, psig	300	400	500	500
Temperature, °C	420	420	420	416
Hydrogen–oil ratio, SCF/B	500	500	500	3900
Vaporization, % vol				
Andrews apparatus	52	37	26	57
Flash still	55	43	34	60

The results on both types of feedstock show that reasonable agreement exists between the two units. If pressure–vaporization plots are made with the gas oil data the curves for each unit are similar in shape, with a tendency to diverge at low vaporizations. The errors of measurement of liquid phase which occur with the Andrews apparatus probably account for this divergence.

From the results obtained in this commissioning work, it was concluded that satisfactory operation could be achieved with the flash still, and experimental programmes were started. Most of the subsequent

* Defined as the absolute difference between two vaporization values.

experimental work done on the flash still answered queries on the phase relationships existing under specific process conditions with a specific feedstock. Thus no opportunity occurred to investigate any one

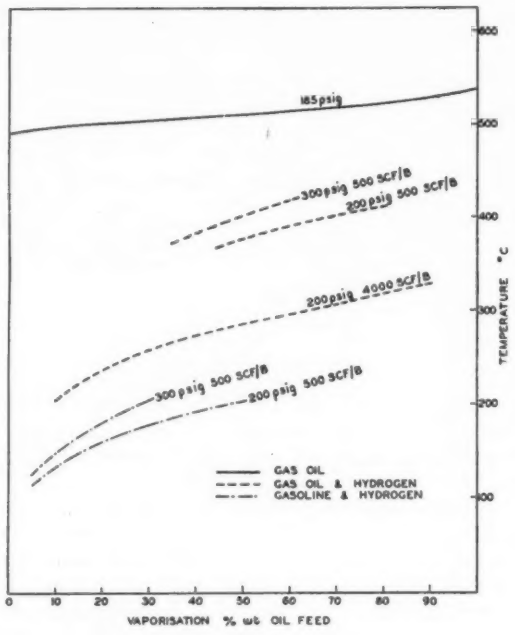


FIG 4

PHASE RELATIONS OF DISTILLATES

feedstock over a full range of temperature, pressure, and hydrogen–oil ratio. The experimental results reported here can only indicate the effects on various feedstocks of altering operating conditions over limited ranges. The effects are described for distillate, crude oil, and residual feedstocks.

(1) *Distillates*

Two distillates were investigated rather more extensively than normally:

(*a*) A Middle East straight run gas oil of 0·8475 specific gravity (60° F/60° F) and 240° to 384° C boiling range (ASTM).

(*b*) A gasoline of 0·8095 specific gravity (60° F/60° F) and 40° to 193° C boiling range (ASTM) produced by steam cracking of a light distillate.

Fig 4 shows the effects of pressure, temperature, and hydrogen–oil ratio on these two distillates. The equilibrium flash vaporization curves, or parts thereof, exhibit the same shape and are approximately parallel to one another, irrespective of pressure or hydrogen–oil ratio. Increase of temperature or hydrogen–oil ratio and decrease of pressure all favour increased vaporization. This is, of course, similar to the phase behaviour of hydrocarbon systems under non-critical conditions. However, it is interesting to compare these curves with the typical equilibrium flash vaporization curve at 185 psig for the gas oil alone, which is included in Fig 4. Due to the design of the flash still, experimental data could not be used for this curve, and it was therefore calculated using a rigorous method of calculation and equilibrium vaporization constants derived from published data.[2,3] The main effect of including hydrogen is to reduce considerably the temperature at which vaporization occurs. Hence the hydrogen acts mainly as an inert gas which exerts a high partial pressure and reduces the partial pressure of the hydrocarbon component of the system. However, the shape of the curve for hydrogen–oil mixtures differs from that of the gas oil alone, both in shape of the near-linear portion and in change of slope at low vaporization. This is probably due to the continually increasing partial pressure of hydrogen as vaporization decreases, condensation being, in effect, inhibited by the lower oil partial pressure.

(2) *Residues and Crude Oils*

Fig 5 presents curves obtained from experimental data on crude oil and residue. The crude oil is typical

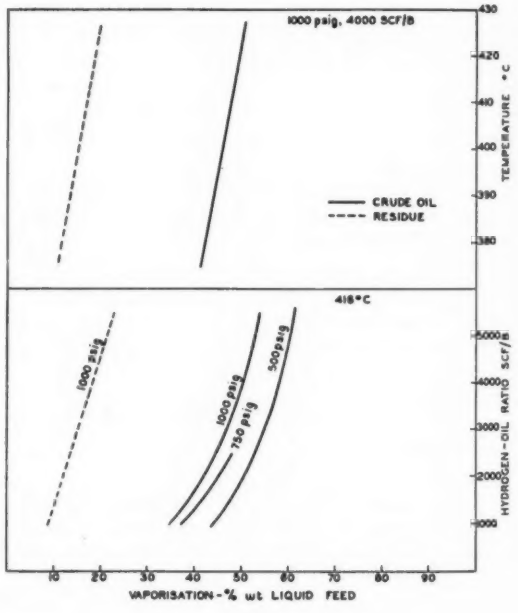


FIG 5

PHASE RELATIONS OF CRUDE OIL AND RESIDUE

of a Middle East crude processed in U.K. refineries and the residue is a refinery product derived from the same crude in a yield of approximately 53 per cent volume.

It will be seen that, in the ranges covered, a linear relationship exists between vaporization and temperature for both crude oil and residue and between vaporization and hydrogen–oil ratio for residue alone. In all cases vaporization increases as the temperature or hydrogen–oil ratio is increased, and the plots between vaporization and hydrogen–oil ratio for crude oil indicate that increase of pressure decreases vaporization. The position of the curves suggests that the pressure effect decreases at the higher pressures.

Comparison of Figs 4 and 5 shows that changes in system conditions have less effect on crude oil and residue feedstocks than on gas oil feedstocks. This would be expected in view of the wide boiling range of the crude oil and residue feedstocks.

DEVELOPMENT OF METHOD OF CALCULATION

(1) *Gas Oil Feedstocks*

When sufficient experimental data became available to construct an equilibrium flash vaporization curve for a Middle East gas oil at 200 psig and 4000 SCF/B hydrogen–oil ratio, a similar curve was calculated by the following method:

(*a*) The true boiling point curve of the gas oil is split into five components and the molar proportion of each component calculated using molecular weight–boiling point relationships. The molar proportion of hydrogen is added to these and a molar distribution of the six-component system obtained.

(*b*) Equilibrium vaporization constants are obtained for hydrogen and for each gas oil component at the system pressure and temperature. The equilibrium vaporization constants used for hydrogen are based on unpublished data and for the gas oil components on data derived from two sources.[2, 3]

(*c*) For each component the proportion present in the liquid phase is calculated from the expression:

$$L_c = \frac{m_c}{1 + \frac{V}{L}K}$$

where L_c = mol of component in liquid phase;
m_c = total mol of component;
V = mol of vapour present in total system;
L = mol of liquid present in total system;
K = equilibrium vaporization constant of component.

As the ratio V/L is unknown, a value is assumed for the purpose of calculation.

(*d*) Summation of the six values for L_c gives a value for L; V can then be obtained by subtracting L from the total number of mol in the system, and the ratio V/L obtained. For true solution this must be identical with the assumed value.

(*e*) If the assumed and calculated V/L ratios differ, further calculations on a trial-and-error basis must be made. Graphical solution can be applied when sufficient data are available, with a final arithmetical check, which should agree within one per cent.

(*f*) When the correct solution is attained, the values for L_c and m_c can be converted to a weight basis and the vaporization value obtained.

(*g*) The calculation is repeated for other system temperatures until sufficient points have been obtained to draw an equilibrium flash vaporization curve.

The equilibrium flash vaporization curve so obtained is shown in Fig 6, together with the curve obtained

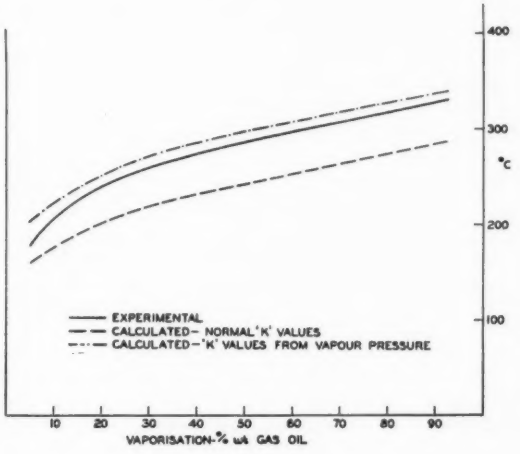


FIG 6

EQUILIBRIUM FLASH VAPORIZATION CURVE FOR GAS OIL AND HYDROGEN AT 200 psig, 4000 SCF/B

experimentally. The discrepancy is obvious. However, the two curves are similar in shape over most of the range, suggesting that the method of calculation is satisfactory but that the equilibrium vaporization values selected are not suitable for this type of system.

In the course of calculation it had been noticed that, of the total hydrogen present, less than 0·2 per cent mol appeared in the liquid phase. Thus, hydrogen acted mainly as an inert and exerted a considerable partial pressure. In such a case the oil partial pressure should be low and the oil vapour would behave as an ideal gas. If this were so, the equilibrium vaporization constants for oil components could be

calculated from normal vapour pressure charts according to:

$$K = \frac{p}{P}$$

where p = vapour pressure of component at system temperature;
P = total system pressure.

Using these equilibrium vaporization constants and the method of calculation previously described, the equilibrium flash vaporization curve was again calculated and is included in Fig 6. Agreement with the experimental curve is obviously much better and can be considered reasonably satisfactory.

This agreement was obtained for a set of system conditions in which temperature was the only variable and where pressure and hydrogen–oil ratio favoured a low oil partial pressure. The method of calculation was therefore tested against experimental data obtained on a different gas oil at system conditions which did not favour low oil partial pressure. The operating conditions and results are summarized in Table IV, together with calculated partial pressures of oil in the vapour phase.

TABLE IV

Vaporization of Gas Oil at 420° C

Specific gravity (60° F/60° F)—0·8630
Boiling range (ASTM) —190° to 356° C

System conditions			Vaporization values, % wt		Partial pressure of oil in vapour phase, psi abs
Temperature, ° C	Pressure, psig	Hydrogen–oil ratio, SCF/B	Experimental	Calculated	
420	200	500	75·2	76·1	93·3
420	400	500	42·7	32·4	107·0
420	800	500	20·3	13·3	120·9

Once more the vaporization values show reasonable agreement, while the partial pressures show that hydrogen does act mainly as an inert.

As further experimental data became available, this method of calculation was checked further. A total of 27 calculated values all agreed reasonably with experimental data and covered a range of four gas oils of different boiling range, 200 to 1000 psig, 200° to 420° C, and hydrogen–oil ratios of 500 to 6000 SCF/B. The maximum variation between experimental and calculated values was 15·7 and the arithmetic mean variation was 7·4. Fig 7 presents a plot of these values, together with a free-hand curve indicating the trend of the points.

The arithmetic mean variation is somewhat in excess of the short term repeatability of 5·0 for hourly experimental vaporization values and could with advantage be reduced. This could be done in two ways:

(i) Formulate suitable equilibrium vaporization constants either experimentally or by suitable correction of existing data.

(ii) Apply an empirical correction to the calculated values.

The first of these courses would be time-consuming whichever method was used. The basis for the second course is already present in the form of the curve drawn in Fig 7. By correcting calculated values to the experimental values according to the curve, large variations will be smoothed out. Applying this correction to the 27 calculated values, the maximum variation is reduced to 8·0 and the arithmetic mean variation to 2·7. It is considered that this correction

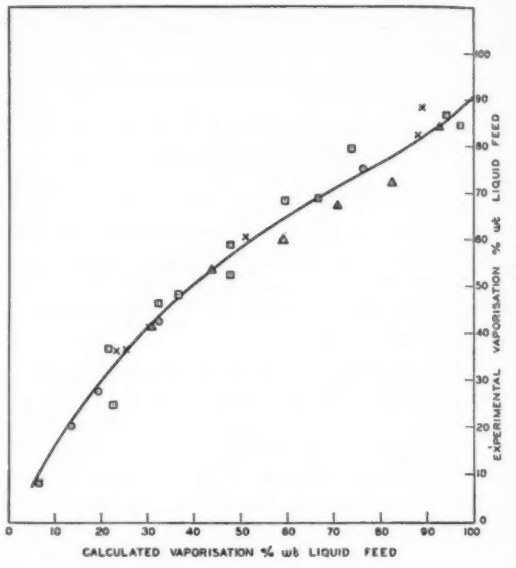


FIG 7

CORRELATION OF EXPERIMENTAL AND CALCULATED VAPORIZATION VALUES FOR GAS OILS

is sufficiently precise for normal chemical engineering design, and the formulation of more suitable equilibrium vaporization constants is not justified at present.

Many hydro-refining processes utilize hydrogen which is contaminated with methane, ethane, and propane. Insufficient experimental data have been collected to enable the above method of calculation to be corrected for contaminated hydrogen streams. Hence it is assumed at present in process design work that such contaminated streams act in a similar manner to pure hydrogen streams.

(2) *Gasoline Feedstocks*

Experimental work on gasoline feedstocks has not been as comprehensive as that on gas oils; only two gasolines were investigated, and the range of operating conditions covered 150 to 450 psig, 100° to 200° C, and only one hydrogen–oil ratio of 500 SCF/B. Vaporiza-

tion values were calculated, corresponding to the 21 experimental values obtained. In this case the gasolines were split into 10 components because of the normal irregularities which exist in gasoline distillation curves; equilibrium vaporization constants for the gasoline components were derived from vapour pressure charts and the method of calculation previously described was used. Experimental and calculated results agreed well, the maximum variation being 1·8 and the arithmetic mean variation 0·8. This is within the short term repeatability for hourly vaporization values, and therefore needs no empirical correction for use in normal chemical engineering design problems. Extrapolation of the experimental data suggested the use of an empirical correction for vaporization values above 60 per cent weight. The correction can be expressed by the equation:

$$y = 1{\cdot}05x - 1$$

where y = corrected vaporization value;
x = calculated vaporization value.

Lack of experimental evidence prevented this correction from being definitely established. For the same reason the good agreement between experimental and calculated results strictly applies to one hydrogen–oil ratio only and should not be used for hydrogen–oil ratios which are very far removed from this value.

(3) *Crude Oil and Residual Feedstocks*

Experimental work on these feedstocks was again not as comprehensive as on gas oil feedstocks. Only one crude oil and two virtually identical residues were used. The temperature range was limited to 416° to 432° C but the pressure and hydrogen–oil ratio ranges were respectively 500 to 3000 psig and 1000 to 6000 SCF/B. Operations at 3000 psig were not done in the described unit but in a high pressure hydrogenation unit suitably modified. They have been included in this work only to extend the range of application.

Vaporization values were calculated, corresponding to 15 experimental values obtained. The true boiling point curves of the residues were determined by normal distillation as far as possible; the resulting residue was then placed on the crude current at the time by analytical data and the upper portion of the crude distillation curve used. Equilibrium vaporization constants for the oil components were again derived from vapour pressure charts; for hydrogen at 3000 psig, the normal charts were extrapolated and gave good agreement at 2000 psig with published data.[4] In spite of these necessary assumptions and extrapolations, the experimental and calculated vaporization values agreed very well, the maximum variation being 7·0 and the arithmetic mean variation 4·3. In all cases the variation was in the same direction, the experimental value being higher. Hence by applying a positive correction of 4·3 to the calculated values, a reduction in variation could be obtained, amounting to a maximum variation of 2·7 and an arithmetic mean variation of 1·1. This correction strictly applies to a limited temperature range, but could possibly be used over a slightly wider range.

The method of calculation and the empirical corrections for different feedstocks described above together form the basis for a method of estimating the phase relationships of a wide range of petroleum fractions when they are in contact with hydrogen at high pressures. The method of calculation and the equilibrium vaporization constants used suggest that the reported limits are not absolute and could be extended, except possibly in the case of hydrogen–oil ratio reduction, when "ideal" equilibrium vaporization constants would not be applicable. The use of different empirical corrections for different feedstocks reduces flexibility of the method to some extent, but reasonable precision can be obtained without using correction factors. The application of this method of calculation to dew-points, bubble-points, or vaporization values close to them cannot be verified experimentally in the present equipment. In spite of this, there will be many applications in hydrogenation processes where it will be of some use.

ACKNOWLEDGMENT

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TECHNICAL NOTE

FORMULÆ FOR CALCULATION OF LEAN MIXTURE KNOCKING CHARACTERISTICS OF AVIATION GASOLINES *

By RAOUL NIKLASSON †

WITH reference to the formula for calculation of lean mixture knocking characteristics of aviation gasoline grade 100/130, published in the *Journal of the Institute of Petroleum*, 1959, **45**, 320, the analogous formulæ for aviation gasolines grades 80, 91/96, 108/135, and 115/145 are presented.

The calculated values correspond to the Aviation Method ASTM D614 and are expressed in performance numbers for values ≥ 100 and octane numbers for values $\leqq 100$.

Formulæ

80 grade

Knock value = 72 × specific gravity at 20° C + $\frac{1}{10}$ × sum of distillation temperatures (° C) at 10 and 50 per cent evaporated + $\frac{3}{10}$ × aniline point (° C)

91/96 grade

Knock value = 90 × specific gravity at 20° C + $\frac{1}{10}$ × sum of distillation temperatures (° C) at 10 and 50 per cent evaporated + $\frac{3}{10}$ × aniline point (° C) − 20 × TEL content (vol per cent)

108/135 grade

Knock value = 108 × specific gravity at 20° C + $\frac{1}{10}$ × sum of distillation temperatures (° C) at 10 and 50 per cent evaporated + $\frac{3}{10}$ × aniline point (° C) − 25 × TEL content (vol per cent)

115/145 grade

Knock value = 117 × specific gravity at 20° C + $\frac{1}{10}$ × sum of distillation temperatures (° C) at 10 and 50 per cent evaporated + $\frac{3}{10}$ × aniline point (° C) − 20 × TEL content (vol per cent)

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† Linköping, Sweden.

COMMENTS ON THE FORMULA FOR CALCULATION OF LEAN MIXTURE KNOCKING CHARACTERISTICS OF AVIATION GASOLINE GRADE 100/130[1,*]

By J. R. LODWICK† (Associate Fellow)

NIKLASSON'S FORMULA

KNOCK value = 100 × specific gravity at 20° C + 1/10 × sum of distillation temperatures (° C) at 10 and 50 per cent evaporated + 3/10 × aniline point (° C) − 20 × TEL content (volume per cent).

The formula has been assessed using data obtained on 40 samples of 100/130 grade aviation gasoline derived from various sources (Table I). It gave values ranging from 1·3 performance number above to 4·0 performance numbers below the determined values. On average the calculated performance number is 1·45 units below the determined value.

Some concern is felt because the formula for a particular sample postulates a decrease in the calculated lean mixture rating as the TEL content increases.

The data presented illustrate the very limited use of the formula to calculate knock ratings of aviation gasolines. No doubt formulæ can be derived to suit the production of a particular grade of a specific production type, but no one formula will suit all blend compositions. It is concluded therefore that the Niklasson formula should be used with caution.

TABLE I

Comparison between Calculated and Experimental Lean Mixture Ratings

Calc No.	Specific gravity			10% + 50% Evaporated temp		Aniline point, ° C		TEL content		Lean mixture ratings, PN		Deviation
	60° F/ 60° F	20° C/ 60° F	100 × sp gr at 20° C/ 60° F	1 ×	1/10 ×	1 ×	3/10 ×	ml/IG	20 × % vol	Aviation method	Calculated value	Above + Below −
1	0·7240	0·72032	72·03	161	16·10	50·8	15·24	3·62	1·59	100·8	101·8	+1·0
2	0·7170	0·71332	71·33	152·5	15·25	51·8	15·54	3·59	1·58	102·8	100·5	−2·3
3	0·7170	0·71332	71·33	158	15·80	53·4	16·02	2·95	1·30	103·2	101·9	−1·3
4	0·7155	0·71174	71·17	152·5	15·25	50·4	15·12	3·50	1·54	102·4	100·0	−2·4
5	0·7195	0·71582	71·58	150·5	15·05	48·6	14·58	3·52	1·55	99·0	99·7	+0·7
6	0·7170	0·71332	71·33	155·5	15·55	53·8	16·14	3·00	1·32	102·0	101·7	−0·3
7	0·7175	0·71382	71·38	158	15·80	53·0	15·90	3·00	1·32	103·2	101·8	−1·4
8	0·7205	0·71682	71·68	152·5	15·25	49·1	14·73	3·65	1·60	101·6	100·1	−1·5
9	0·7190	0·71532	71·53	157	15·70	52·4	15·72	3·69	1·62	101·6	101·3	−0·3
10	0·7205	0·71682	71·68	155·5	15·55	51·0	15·30	3·59	1·58	101·2	101·0	−0·2
11	0·7195	0·71582	71·58	156·5	15·65	51·4	15·42	3·65	1·60	100·0	101·0	+1·0
12	0·7245	0·72082	72·08	164·5	16·45	49·3	14·79	3·59	1·58	100·8	101·7	+0·9
13	0·7240	0·72032	72·03	162	16·20	49·2	14·76	3·49	1·53	102·4	101·5	−0·9
14	0·7240	0·72032	72·03	163	16·30	48·3	14·49	3·52	1·55	100·0	101·3	+1·3
15	0·7245	0·72082	72·08	162	16·20	48·3	14·49	3·56	1·57	102·0	101·2	−0·8
16	0·7250	0·72132	72·13	161	16·10	47·8	14·34	3·59	1·58	102·4	101·0	−1·4
17	0·7080	0·70424	70·42	155·5	15·55	62·2	18·66	5·71	2·51	105·0	102·1	−2·9
18	0·7265	0·72282	72·28	162	16·20	48·4	14·52	3·50	1·54	102·8	101·5	−1·3
19	0·7260	0·72232	72·23	161	16·10	48·3	14·49	3·49	1·53	102·8	101·3	−1·5
20	0·7260	0·72232	72·23	165	16·50	48·3	14·49	3·48	1·53	102·4	101·7	−0·7
21	0·7245	0·72082	72·08	163·5	16·35	49·7	14·91	3·47	1·53	102·4	101·8	−0·6
22	0·7245	0·72082	72·08	161·5	16·15	49·4	14·82	3·50	1·54	103·2	101·5	−1·7
23	0·7280	0·72432	72·43	169·5	16·95	48·9	14·67	3·60	1·58	105·0	102·5	−2·5
24	0·7260	0·72232	72·23	169	16·90	49·3	14·79	3·56	1·57	102·8	102·4	−0·4
25	0·7220	0·71832	71·83	153	15·30	48·5	14·55	5·37	2·36	102·8	99·3	−3·5
26	0·7225	0·71882	71·88	153·5	15·35	48·7	14·61	5·30	2·33	102·8	99·5	−3·3
27	0·7185	0·71482	71·48	157·5	15·75	51·9	15·57	4·97	2·19	104·3	100·6	−3·7
28	0·7150	0·71124	71·12	164·5	16·45	61·8	18·54	5·36	2·36	105·4	103·8	−1·6
29	0·7260	0·72232	72·23	163	16·30	48·7	14·61	5·43	2·39	102·8	100·8	−2·0
30	0·7150	0·71124	71·12	163·5	16·35	61·6	18·48	5·44	2·39	104·7	103·6	−1·1
31	0·7155	0·71174	71·17	156·5	15·65	55·5	16·65	5·20	2·29	101·2	101·2	—
32	0·7205	0·71682	71·68	162·5	16·25	49·1	14·73	3·56	1·57	101·2	101·1	−0·1
33	0·7115	0·70784	70·78	157	15·70	56·1	16·83	3·44	1·51	105·0	101·8	−3·2
34	0·7185	0·71482	71·48	155·5	15·55	50·4	15·12	3·54	1·56	104·0	100·6	−3·4
35	0·7175	0·71382	71·38	153·5	15·35	50·2	15·06	3·49	1·54	104·3	100·3	−4·0
36	0·7190	0·71532	71·53	152	15·20	48·3	14·49	3·60	1·58	102·8	99·6	−3·2
37	0·7075	0·70374	70·37	152·5	15·25	57·8	17·34	3·60	1·58	105·4	101·4	−4·0
38	0·7140	0·71024	71·02	155·5	15·55	52·8	15·84	3·60	1·58	102·8	100·8	−2·0
39	0·7170	0·71332	71·33	154	15·40	50·5	15·15	3·60	1·58	100·4	100·3	−0·1
40	0·7190	0·71532	71·53	152	15·20	48·3	14·49	3·60	1·58	102·8	99·6	−3·2

* MS received 16 December 1959.

† The British Petroleum Co. Ltd.

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VISCOSITY TEMPERATURE CHARACTERISTICS OF OILS *

By A. CAMERON †

SUMMARY

Most of the standard viscosity temperature laws require that $\left(-\frac{1}{\eta}\cdot\frac{d\eta}{dt}\right)$ should be a simple function of the temperature. This is studied and found not to hold outside a limited temperature range.

A much better correlation is obtained by plotting the logarithm of the derivative

$$\log\left(\frac{d\eta}{dt}\right) \text{ against } \log(\eta)$$

The significance of this for an index of viscosity is discussed.

INTRODUCTION

It has been known for some time [1] that almost all the standard viscosity temperature laws are based on the solution of a single differential equation. In order to assess the possibilities of a wide range viscosity temperature law, the validity of this equation is naturally of importance. In this paper a study is made of this, using viscosity temperature data recently available.

The differential equation is

$$-\frac{d\eta}{\eta dt} = \frac{1}{T}$$

where η = viscosity;
t = temperature;

and T is a polynomial in temperature, t, of the form $(a + bt + ct^2 + \ldots + nt^m)$. Most of the standard equations can be derived by retaining different numbers of terms in this polynomial.

STANDARD VISCOSITY EQUATIONS

If the first term only is retained, *i.e.* $-\frac{d\eta}{\eta dt} = a$, then integration gives $\eta = k\exp(-at)$, which is Reynolds' equation.[2] This holds only for a limited range.

Keeping in the second term and rewriting so that $T = a + bt = \frac{0 + t}{m}$, where $a = 0/m$ and $b = 1/m$. The equation becomes

$$-\frac{d\eta}{\eta dt} = \frac{m}{t + 0}, \text{ giving } \eta = \frac{k}{(t + 0)^m}$$

This is Slotte's equation.[3] It is sometimes useful in calculations, as it avoids the exponential, which occurs in the others. It is found that if t is in degrees Fahrenheit, 0 can be put equal to zero.

Next, if the polynomial includes the squared term, but the constants are such that

$$T = \frac{(0 + t)^2}{B}, \text{ i.e. } a = \frac{0^2}{B}, b = \frac{20}{B}, \text{ and } c = \frac{1}{B}$$

then $\eta = ke^{\frac{B}{t + 0}}$.

This equation is due to Vogel,[4] and when t is in degrees Centigrade, 0 can be put equal to 95.

The next equation does not quite fit into this pattern, but does not differ widely from it. There only one term of the polynomial is kept, *i.e.* $T = nt^m$. The left-hand side of the equation is rewritten, by defining $Z = \eta + \alpha$, where α is a constant.

Then the equation reads

$$-\frac{dZ}{Zdt} = \frac{1}{nt^m}$$

It integrates to $(\eta + \alpha) = ke^{\frac{1}{nt}}$. This formula is due to Walther.[5] Here the viscosity is usually in centistokes and the constant α can be 0·6 or 0·8. The difference for lubricating oils is not serious, as Nissan [6] has shown.

Finally, there is a post-war Russian formula [7] with a somewhat different right-hand side in the differential equation. This viscosity equation is

$$\sqrt{\log \eta} = \left(a + \frac{b}{t}\right)$$

if it is squared and differentiated, then

$$-\frac{d\eta}{\eta dt} = \frac{2b}{t^2}\left(a + \frac{b}{t}\right)$$

In this case also the right-hand side of the differential equation is a function of t.

Up to now this analysis has shown that all the viscosity temperature laws depend on the validity of the relation $-\frac{d\eta}{\eta dt} = \frac{1}{f(t)}$, where $f(t)$ is some function

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of the temperature, usually a polynomial in t. Thus, if the reciprocal $-\eta \frac{dt}{d\eta}$ is obtained and plotted against temperature the validity of the various approximations can be studied.

VISCOSITY DERIVATIVE

There has appeared comparatively recently very full data on the viscosity of oils taken at regular

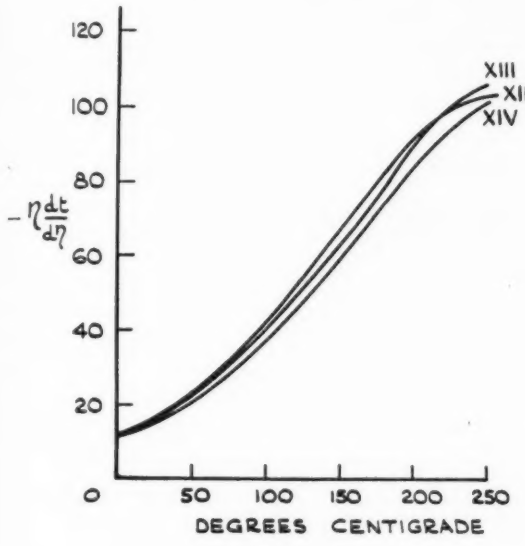

FIG 1

temperature intervals, 50° C apart, between 0° and 250° C. These viscosities were determined by Weber and are quoted by Rost.[8] The fact that the viscosities are at equal temperature intervals enables the temperature derivative to be obtained by numerical differentiation.

This was done by Bickley's six-point formula,[9] which is extremely accurate, *i.e.* better than $\frac{1}{4}$ of the sixth difference. It is at least as accurate as the measurements themselves. By differentiating the logarithm the value of $\left(\frac{d\eta}{\eta dt}\right)$ is found direct as

$$\frac{d(\log_e \eta)}{dt} = \frac{1}{\eta}\frac{d\eta}{dt}$$

Some sample results are plotted in Fig 1, the Roman numbers being Rost's reference numbers. It is seen straight away that at high temperatures the curves do not follow a regular pattern. Thus any of the previous approximations, *i.e.* that $\eta \frac{dt}{d\eta}$ is proportional to (a), $(a + t)$, $(a + t)^2$, t^m, or $t^3/(a + t)$ cannot represent a curve of this type. To achieve this an expression of the type $(a + bt + ct^2 + dt^3 + \ldots)$ would be necessary. This again would not suffice, as the curves are not all of the same type.

At this point it became clear that no further progress could be made along these lines. The viscosity gradient itself, $d\eta/dt$, was then plotted against the temperature, t, with no success.

VISCOSITY DERIVATIVE VERSUS VISCOSITY

Finally, the gradient, $d\eta/dt$, was plotted against the viscosity. This is shown in Fig 2, where both quantities are plotted logarithmically. It is clear that there is a good correlation. It shows that the value of the temperature derivative $d\eta/dt$ is primarily determined by the value of the viscosity itself. The relation between log $(d\eta/dt)$ and log η is in fact nearly linear. An equation which fits the results is

$$\log_{10}(d(cP)/-dt) = -3{\cdot}9 + 1{\cdot}460 \log_{10}(cP) - 0{\cdot}13e^{\cdot 443 \log_{10}(cP)}$$

or

$$-\frac{d\eta}{dt} = 0{\cdot}00101\eta^{1{\cdot}46}e^{-(\cdot 71\eta^{\cdot 192})}$$

where (cP) is viscosity in centipoises and η viscosity in poises

This equation, if integrated up (which it can be in terms of the incomplete gamma-function), gives the temperature as a function of the viscosity, *i.e.* $t = f(\eta)$, instead of the usual equations where viscosity is a function of temperature, $\eta = f(t)$.

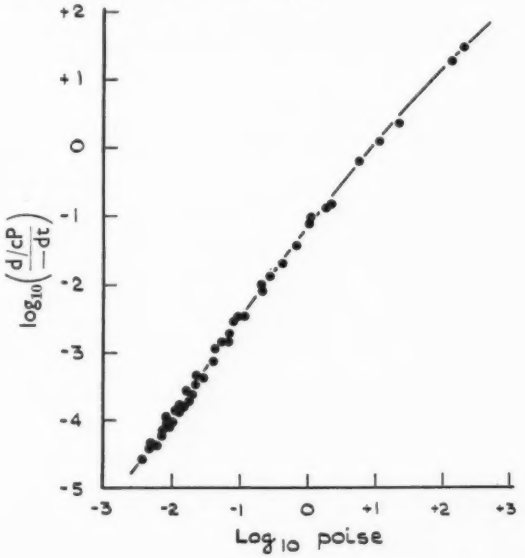

FIG 2

As it stands this graph ignores the different viscosity indexes of individual oils. This comes about because the range is so great, from 0·004 to 210 poises, that the individual variations are submerged, as they are of second order. These second order variations, however, are clearly of prime commercial importance.

It is seen, therefore, that to obtain a significant figure for the index of viscosity of an oil, this first order effect—that $d\eta/dt$ is mainly determined by η alone—must be allowed for and removed. This is the starting point of the index of viscosity proposed in the companion paper to this, based on the modified Vogel equation, which is of course limited by the accuracy of that equation.

Work is now going on to see if a basic law can be obtained using a suitable reference oil. This will give $d\eta/dt$ as a function of the viscosity itself and will be obtained over as wide a range as possible. This relation could then be used as a standard, with which other oils could be compared, and from which an empirical wide range chart could be constructed.

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See also "Anomalous Viscosity of Oils and its Influence on Friction in Machines." Publ. No. 55, Ministry of Auto and Tractor Industry, U.S.S.R. (NAMI) Mashgiz, Moscow, 1949, §23, Equation 25.

AN INDEX OF VISCOSITY *

By A. CAMERON †

SUMMARY

The modified Vogel equation

$$\eta = k \exp\left(\frac{b}{t + 95}\right)$$

is described and its main characteristics considered. It is shown that for 0 vi oils the exponent b is dependent only on the viscosity at a given temperature, here 100° F, and is expressed by the relation

$$b_o = 184 + 450 \log_{10} \nu$$

where ν is the kinematic viscosity in centistokes at 100° F. If any other oil has the same viscosity at 100° F but a different value of b, as it will if its vi is not zero, then the R-rating is defined as

$$R = \left(\frac{b_o - 1}{b}\right) 1000$$

†this is applied to oils of 100 vi the thicker oils have a higher R-rating.

INTRODUCTION

THERE have been many attempts to find an alternative to the very well established Dean and Davis viscosity index. None has been successful as the two requirements that (1) the law on which it is based must have a very wide range of application, and (2) the index must give a single value for oils of comparable "goodness," however widely different their viscosities, are very hard to meet.

The method proposed here is derived from a viscosity temperature law that is of comparable accuracy to the Walther–ASTM law on which the ASTM chart is based. Its advantage, however, is that it follows directly from the viscosity temperature law and is based on the lower limit of the viscosity index oils, in fact on the 0 vi series. Its upper limit is therefore not bounded. Furthermore, it can be derived directly from any chart drawn from this modified Vogel formula.

MODIFIED VOGEL EQUATION

In 1945 the author [1] in a paper to the IP, showed that the Vogel [2] viscosity equation, which is

$$\eta = k \exp\left(\frac{b}{t + \theta}\right)$$

where η = viscosity;
t = temperature;
k, b, θ = constants for any oil,

could be simplified without serious loss of accuracy by putting θ equal to 95, when t was in ° C.

The equation so modified has been used a certain amount in Germany, where it is known as the Vogel–Cameron formula. In particular, Rost,[3] in a series of papers, has shown that it is as accurate as the standard Walther law, which is the basis of the ASTM chart.

This Vogel–Cameron formula has several advantages over the ASTM–Walther equation. First, the two

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constants k and b are quite distinct in their meaning. If t is in a given temperature scale, say Centigrade, then b is the measure of the temperature dependence of the viscosity. The units of b are also of temperature so the ratio $b/(t + \theta)$ is dimensionless. The constant k is the "thickness" of the oil, and it has the same units as those of the viscosity it describes. Thus, changing the viscosity from poises to Reyns changes k by the standard conversion factor of $1{\cdot}45 \times 10^{-5}$, but leaves b untouched.

Furthermore, as this is a straight exponential law, the viscosity ordinate is pure logarithmic. Thus a given size of graph paper can cover a wide viscosity scale, as the decimal point can be shifted to suit the range of oil under consideration.

ROST'S TEMPERATURE VISCOSITY NUMBER

Rost also shows that if a large number of oils is measured, the temperature viscosity constant b varies with the viscosity itself.

If the viscosity of the oil was measured at a given temperature, say 50° C, then an average value of b, b_{av}, over a large number of oils was given by the relation

$$b_{av} = 400 \log_{10} \eta_{50} + 297{\cdot}9$$

where b_{av} = average value of b;
η_{50} = viscosity of oil in centipoises at 50° C.

This can be written

$$b_{av} = 400 (\log_{10} \eta_{50} - \log_{10} 0{\cdot}18)$$
$$= 400 \log_{10} (\eta_{50}/\eta_x)$$

where $\eta_x = 0{\cdot}18$, a constant.

This constant indicates that at a given high temperature all oils tend to the same viscosity of 0·18 cP. The temperature is 773·6° C, so this prediction is reasonably safe from experimental verification.

Rost gives a temperature–viscosity number G, which is that ratio of the actually measured or determined value of b for an unknown oil, to the average b_{av}, *i.e.* $G = b/b_{av}$.

This concept will be extended in the following way.

INDEX OF VISCOSITY

If the oils used by Rost are studied carefully there is quite a scatter in the values of his b_{av}. It seemed worth studying how oils of the same vi would behave. His system was slightly changed in that the reference viscosity temperature was taken at 100° F (37·78° C) instead of 50° C (122° F). The viscosity at 100° F was based on centistokes not centipoises; this will be clear later.

The values of b can be obtained from the viscosity in centistokes at two temperatures quite easily as the coefficient of volume expansion of all oils is nearly the same at $7{\cdot}4 \times 10^{-4}$ per ° C.

The value of b was worked out for all the 0 vi oils listed in the standard tables and plotted against the corresponding viscosity in centistokes at 100° F. The values of b so calculated were all found to lie on a single exponential line (Fig 1).

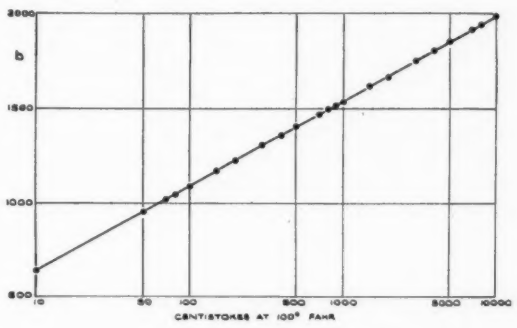

FIG 1
b AGAINST VISCOSITY AT 100° F FOR 0 VI OILS

The line has very little scatter in it and it is from this that the reference or base value of b is defined. It means that any oil of 0 vi has a viscosity temperature exponent, which is related to its viscosity at 100° F. The equation expressing this relation between the value of b, which will be called b_o, and the viscosity in centistokes at 100° F, which will be designated ν, is

$$b_o = 184 + 450 \log_{10} \nu \quad . \quad . \quad . \quad (1)$$

This provides a method for obtaining an index of viscosity.

First, the b value for any given oil is calculated. The method of doing this from the kinematic viscosity at 100° and 210° F is given in the appendix. The value so obtained is compared with the value of b_o for a zero vi oil of the same viscosity at 100° F. The resulting ratio is an indication of the change of viscosity with temperature.

In order to have numbers similar in magnitude to the standard vi the ratio R is defined as follows.

$$R = \left(\frac{b_o}{b} - 1\right) 1000 \quad . \quad . \quad . \quad (2)$$

where b_o is calculated from equation (1) and b is calculated for the unknown oil. For 0 vi oils $R = 0$, by definition.

A number of R values have been calculated out for a series of 100 vi oils. These are shown in Fig 2. The R values are plotted on the ordinate against the viscosity at 100° F on the abscissa.

What is interesting is that the 100 vi series of oils have a higher R-rating the higher the 100° F viscosity.

This fits in with the known fact that the higher the viscosity, the harder it is to obtain a high vi. On the R-rating an oil of 100 vi of 10 cS at 100° F rates 34,

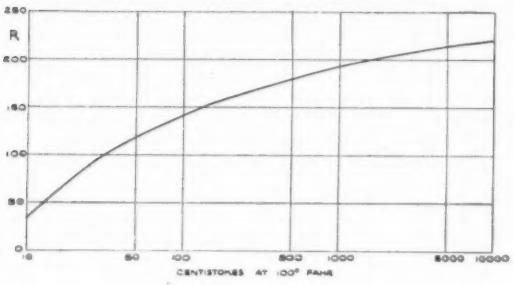

FIG 2

R FOR 100 VI OILS AGAINST VISCOSITY AT 100° F

at $32\frac{1}{2}$ cS at 100° F, it rates 100, and if it is 500 cS at 100° F it rates 180.

CONCLUSION

What has been done is to develop an index of viscosity from a temperature viscosity law whose validity is of the same order as the Walther–ASTM law. Zero is defined from the standard series of 0 vi oils. The upper limit is left free and can go as high as required.

The fact that the index of viscosity comes from the viscosity temperature law means that it can be evaluated directly from a chart based on this law.

APPENDIX

TO OBTAIN b FROM THE RATIO OF THE KINEMATIC VISCOSITIES AT 100° AND 210° C

The viscosity in centipoises can be obtained from the kinematic viscosity in centistokes by multiplying by the density. The density ρ_2 at any temperature t_2 can be obtained from the density ρ_1, at a standard temperature t, from the relation

$$\rho_2 = \rho_1[1 - \alpha(t_2 - t_1)]$$

If t_2 and t_1 are in degrees centigrade then $\alpha = 7{\cdot}4 \times 10^{-4}$ for almost all oils. The two standard temperatures in this work are 100° F (37·78° C) and 210° F (98·89° C).

The Vogel–Cameron formula is $\eta = k \exp\left(\frac{b}{t + 95}\right)$, hence if ν_1 and ν_2 are the two kinematic viscosities at t_1 and t_2, then

$$\eta_1 = \nu_1\rho_1 = k \exp\left(\frac{b}{t_1 + 95}\right)$$

and

$$\eta_2 = \nu_2\rho_1[1 - \alpha(t_2 - t_1)] = k \exp\left(\frac{t_2 + 95}{b}\right)$$

whence

$$\frac{\nu_1}{\nu_2} = [1 - \alpha(t_2 - t_1)]e^{b\left(\frac{1}{t_1+95} - \frac{1}{t_2+95}\right)}$$

Next, t_1 is put equal to 37·78° C (100° F) and t_2 to 98·89° C (210° F). Then multiplying out and taking logarithms which can be converted to base 10

$$\log_{10}\frac{\nu_{100}}{\nu_{210}} = \log_{10}(\cdot 9548) + \frac{b \times 2{\cdot}374 \times 10^{-3}}{2{\cdot}3025}$$

or

$$b = 970 \log_{10}\frac{\nu_{100}}{\nu_{210}} + 19{\cdot}4$$

where ν_{100} is the kinematic viscosity at 100° F;
ν_{210} „ „ „ „ „ 210 F.

The 19·4 is the correction for the change in density of the oil with temperature.

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OBITUARIES

ALAN JAMES RUTHVEN-MURRAY, C.M.G.

1900–1959

As a member of Council for six years, since 1953, Alan Murray had every qualification in the fullest measure. Throughout this time he was fighting a long battle against ill-health. His fortitude showed the strength of character of a man whose career was an outstanding example of a life devoted to the service of his profession.

As a young man he was just old enough to take part in the last years of the 1914–18 war, being commissioned in the Royal Air Force. He then went to Oxford (as befits the grandson of the lexicographer) and read geology. Very soon afterwards he was engaged in his first oil exploration venture, a lengthy spell in the Magdalena Valley of Colombia. It was a rigorous life in an area of swamps, rivers, and dense tropical vegetation. Here he enjoyed the responsibility of an individual assignment and the fascination of mapping the unmapped. Here also he had his initiation into that essential attribute of the profession, the ability to work on the best of terms with the local people, a subject which was to be his continuing interest and preoccupation.

His next assignment took him to Trinidad and his first years there were at a time of exceptional difficulty for the oil industry. The competition of countries with flush production, and the resultant low prices, put many of the Trinidad companies into difficulties. Added to this, the complex geology and the difficult drilling conditions compounded the problems of maintaining solvency. It was a testing period, and the experience that Alan Murray gained at this time was to stand him in good stead later.

The latter part of the 1930s witnessed the renaissance of the Trinidad oil industry. With more rewarding prices and the prospect of improved profits, the companies were able to embark on substantial capital expenditures. Amenities and working conditions were improved and the industry began to assume its present shape of well-ordered efficiency. Alan Murray was at that time the Resident Manager of Kern Trinidad Oilfields. The position demanded both the technical ability necessary to run the diverse operations of an oilfield and it also called for a ready understanding of the human problems arising from an emergent Trade Union movement. For this task Alan Murray had all the qualifications. His somewhat commanding appearance and a penetrating eye tended to conceal the interest he took in the welfare and living conditions of the strangely assorted agglomeration of people that form an oilfield community. It may not, perhaps, be generally realized how much the successful operation of an oilfield in a self-contained area can be due to the conscientious activities of the husband and wife resident in the manager's bungalow. There can hardly have been better examples than Alan Murray and his charming wife. Many will remember the house at Kern, with its collection of hibiscus set among the immortelle trees, and where hospitality was dispensed to all and sundry.

The respect which the Trinidadian workers held for their manager at Kern was no doubt recorded in verse and music in more than one calypso. (And probably including an uproarious stanza describing how on one occasion, when gunning for duck in a fragile craft, the boatman decided it was necessary to leap for safety only to receive the full content of one barrel clean through the nether end.)

The successful managership of Kern led, in 1942, to the offer of the post of General Manager to Trinidad Leaseholds at Pointe-à-Pierre. There followed a period of intense activity, with production, refining, and shipping activities all having to be attuned to the needs of war.

In 1951 there came the appointment of Managing Director of Trinidad Leaseholds Ltd. But recurring bouts of ill-health forced him in due course to seek less onerous duties and he decided to take up consulting work. It was typical of his determination to keep going that he should at this time have taken the calculated risk, as an invalid, of making a personal reconnaissance of an area in the Middle East.

It may be trite to say that a man can do much for the betterment of the world. So also can an industry. In this context Alan Murray's contribution should not go unrecorded.

O. F. T.

ERNEST W. DEAN

1888–1959

ONE of the outstanding figures in the development of petroleum analysis and testing passed away with the death, at the age of 71, of Dr Ernest W. Dean, at his home in Westfield, New Jersey, on 16 October 1959. Apart from the important methods which are associated with his name, his influence on standardization and the examination and testing of petroleum products was great.

Ernest Dean was born at Taunton, Massachusetts, in 1888 and received his B.A. from Clark University in 1908 and his Ph.D. from Yale in 1914. He first worked as an Instructor in Chemistry at Hobart College from 1908 until in 1914 he joined the U.S. Bureau of Mines in Pittsburgh as a junior organic chemist in the Petroleum Section of the Experimental Station. From 1916 to 1922 he was Chief of the Section. In the latter year he left the Bureau of Mines to become Director of the Standard Inspection Laboratory of the Standard Oil Company of New Jersey. He was the third director of the laboratories, the first having been George M. Saybolt, who had retired from the Company in 1919, after many years of service. Dean remained as Director of S.I.L., first in New York and then at Bayonne until early 1950, when the department was merged in the Research Division of the Company. He then joined the administration side of the Standard Oil Development Company (now Esso Research and Engineering Company) until he retired in 1953.

Ernest Dean was a very active member of ASTM, a member of Committee D-2 since 1920, and a member or chairman of many sub-committees, particularly on such subjects as illuminating oils and viscosity. He was elected an Honorary Member of Committee D-2 in 1954. He became a member of the Institute in 1928, and from 1945 was an honorary member of the Institute's Standardization Committee, in recognition of his work in promoting co-operation between the American and British standardization bodies. He found time also to work for other scientific and technical bodies such as the Society of Automotive Engineers, and was a Charter Member and co-organizer of the ACS Division of Petroleum Chemistry.

In the field of petroleum testing, Dean will be remembered particularly for two methods, both of which originated many years ago, but which are still in world-wide use. The first of these, the Dean and Stark method for water determination, was published in *Industrial and Engineering Chemistry* in 1920, while Dean was at the Bureau of Standards, and has been standardized under the designations IP 74 and ASTM D-95.

The well-known Dean and Davis Viscosity Index System is still, in spite of its practical and theoretical limitations, the most useful and widely used of such systems to-day. Ernest Dean first became actively interested in this problem about 1927, and was soon joined in the work by G. H. B. Davis. Together they published an account of the system in *Chemical and Metallurgical Engineering* in 1929. Some modifications of the system were published in 1932 and 1940 by Dean and others, and the revised system has been an ASTM and IP standard for many years (ASTM D-567 and IP 73). In spite of the imperfections of the scale —and Dean himself claimed in recent years that he then could devise a much better system for describing viscosity–temperature relationships—it is in such wide use in both the refining and marketing fields that it will be displaced only by a system which shows very marked practical and theoretical advantages.

His technical achievements ensure to him a place in the history of petroleum science, but Ernest Dean will be remembered by a great number of friends in many countries for his friendliness and helpfulness and his co-operation and enthusiasm in any matter with which he was associated. All his friends would wish to express their sympathy to Mrs Dean and her family.

E. B. E.